MAXIMIZING LIGHT OLEFINS YIELD FROM THE FLUID CATALYTIC CRACKING OF WHOLE CRUDE OIL

BY

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This thesis is dedicated to my family for their support all through my life

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LIST OF ABBREVIATIONS AND NOMENCLATURE

FCC :	Fluid Catalytic Cracking
MAT :	Microactivity Test
ASL :	Arabian Super Light
AXL :	Arabian Extra Light
AL :	Arabian Light
VGO :	Vacuum Gas Oil
E-Cat :	Equilibrium Catalyst
USY :	UltraStable Y zeolite
LPG :	Liquefied Petroleum Gas
LCO :	Light Cycle Oil
HCO :	Heavy Cycle Oil
RON :	Research Octane Number
HTC :	Hydrogen Transfer Coefficient
C/O :	Catalyst to Oil ratio
XRD :	X-ray Diffraction
SEM :	Scanning Electron Microscopy
TPD :	Temperature Programmed Desorption
kij :	Reaction rate constant for reaction of lump i to lump j
ko-ij :	Pre-exponential factor for reaction of lump i to lump j
Eij :	Apparent activation energy for reaction of lump i to lump j
t :	Contact time

tos :	Time on stream
α :	Deactivation constant
φ :	Deactivation function
Yi :	Weight fraction of lump i
T :	Reaction temperature
To :	Average temperature of the experiments
R :	Universal gas constant

ABSTRACT

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Thesis Title : Maximizing Light Olefins Yield from the Fluid Catalytic Cracking of Whole Crude Oil

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The catalytic cracking of three light crude oils (Arabian Super Light –ASL, Arabian Extra Light-AXL and Arabian Light-AL) was carried out in a fixed-bed microactivity test (MAT) unit. This was done to investigate the possibility of using crude oils as feeds in fluid catalytic cracking (FCC) units instead of using conventional vacuum gas oils (VGOs) and also to increase the yield of light olefins using modified ZSM-5 additives. The three crude oils and a hydrotreated VGO were cracked over an equilibrium catalyst (E-Cat) and a blend of E-Cat and 25 wt.% ZSM-5 at 550°C and 1 atm over a range of catalyst oil ratios. The ZSM-5 was physically added to the E-Cat in various ratios and maximum light olefins yield was obtained at 25 wt.% ZSM-5 additive. The product yields obtained were compared at a constant conversion of 60%. Under the same conditions, VGO and the three crude oils yield comparable amount of light olefins (12 wt.%). This suggests that crude oils can be used in place of VGO in fluid catalytic cracking (FCC) units. Cracking over E-Cat/ZSM-5 blends, maximum light olefins yield was obtained on cracking the ZSM-5 with Si/Al molar ratio of 280 (Z280). The total yields of light olefins were 14.5, 21.3 and 20 wt.% for ASL, AXL and AL respectively. Modification of the Z280 additive by Mn-impregnation led to slightly increased light

olefins yields of 14.8, 21.8 and 21.6 wt.% for ASL, AXL and AL crude oils while introduction of mesopores into the Z280 additive by desilication led to increased yields of 15.7, 23 and 21.6 wt.% for ASL, AXL and AL respectively. Further modification of the Z280 additive by steaming led to relatively unchanged light olefins yields; this suggests that the steamed additive is hydrothermally stable under the reaction conditions. For the three crude oils, the aromatics content of the gasoline increased with increasing ZSM-5 acidity with a corresponding increase in GC-RON. The highest gasoline GC-RON was obtained on cracking AL over Z30. Additive modification has no effect on gasoline aromatics content for all the crude oils. A four-lump kinetic model accurately predicted experimental yields of AL cracking over E-Cat and E-Cat/Z280 between 500 °C and 550 °C. From the kinetic model, the apparent activation energy for the conversion of gasoline to gases for AL decreased from 21 kcal/mol over E-Cat to 16 kcal/mol over E-Cat/Z280 which indicates that Z280 facilitated the increased cracking of gasoline-range reactive species to light olefins.

ملخص الرسالة

الاسم الكامل: عثمان عبد الحفيظ

عنوان الرسالة: زيادة إنتاجية الأوليفينات الخفيفة من التكسير الحفزي للموائع للنفط الخام الكلي

التخصص: هندسة كيميائية

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التكسير الحفزي لثلاثة أنواع من النفط الخفيف (العربي شديد الخفة-ASL، العربي الخفيف جداً-AXL و العربي الخفيف-AL) أجريت في وحدة إختبار مثبتة ذات النشاط الصغير للإختبار (MAT). وقد تم ذلك لبحث إمكانية استخدام الزيوت الخام كمغذي في وحدات التكسير المحفز للمائع (FCC) بدلا من استخدام الزيوت الغاز التقليدية (VGOs) وأيضا لزيادة الغلة من الأوليفينات الخفيفة باستخدام إضافات ZSM-5 المعدل. تم تكسير أنواع النفط الخام الثلاثة و زيوت استخدام الزيوت الغاز التقليدية (VGOs) على حفاز التوازن (E-cat) و خليط من حفاز التوازن (E-cat) مع ZSM-5 25% عند درجة حرارة 550 درجة مئوية عند نسب مختلفة للنفط/العامل الحفاز. تم إضافة الZSM-5 فيزيائياً للعامل الحفاز E-Cat بنسب مختلفة وتم الحصول على أقصى قدر من الأوليفينات الخفيفة عند نسبة وزنية 25٪ من ZSM-5 مضافة. وتمت مقارنة عوائد المنتجات التي تم الحصول عليها في تحويل ثابت قدره 60٪. في ظل نفس الظروف، VGO والزيوت الخام الثلاثة تسفر عن كميات مماثلة من الأوليفينات الخفيفة (12 وزن٪). هذا يشير إلى أن النفط الخام يمكن استخدامها في مكان VGO في تكسير وحدات الحفاز المائع (FCC). التكسير على خليط E-Cat/ZSM-5، تم الحصول على الحد الأقصى الأوليفينات الخفيفة على تكسير ZSM-5 بنسبة مولية للسيليكا/ الألومنيا تساوي 280 (Z280). بلغ إجمالي عائدات الأوليفينات الخفيفة وزنياً 14.5، 21.3 و 20٪ من العربي شديد الخفة-ASL، العربي الخفيف جداً-AXL و العربي الخفيف-AL على التوالي. أدى التعديل في Z280 عن طريق تشريب المنغنيز إلى زيادة طفيفة في عوائد الأوليفينات الخفيفة من 14.8، 21.8 و 21.6 وزن٪ لأنواع النفط الخام: العربي شديد الخفة-ASL، العربي الخفيف جداً-AXL و العربي الخفيف-AL على التوالي، في حين أدى إدخال mesopores في إضافة الZ280 عن طريق إزالة السيليكا لزيادة الغلة إلى 15.7، 23 و 21.6 وزن٪ لأنواع النفط الخام: العربي شديد الخفة-ASL، العربي الخفيف جداً-AXL و العربي الخفيف-AL على التوالي. مزيد

من التعديل على Z280 المضاف عن طريق البخار أدى نسبياً إلى عائد ثابت من الأوليفينات الخفيفة. وهذا يشير إلى أن هذه المادة المضافة المعالجة بالبخار مستقرة hydrothermally تحت ظروف التفاعل. بالنسبة لزيوت النفط الخام الثلاثة، ومحتوى المواد العطرية من البنزين زادت مع زيادة الحموضة في ال ZSM-5 مع زيادة مقابلة في GC-RON. تم الحصول على أعلى GC-RON في الغازولين على تكسير الخام العربي الخفيف-AL خلال العامل Z30. تعديل المضافات ليس له أي تأثير على محتوى العطريات في الغازولين لجميع أنواع الزيوت الخام. النموذج الحركي ذو الأربعة تكتلات تنبأ بدقة بالنتائج التجريبية لتكسير النفط العربي الخفيف AL على العامل الحفاز التجاري E-Cat و العامل الحفاز E-Cat/Z280 بين درجات الحرارة 500-550 درجة مئوية. من النموذج الحركي، انخفضت طاقة التنشيط لتحويل الغازولين إلى غازات للنفط العربي الخفيف AL من 21 كيلوكالوري/مول على العامل الحفاز التجاري E-Cat إلى 16 كيلوكالوري/مول على العامل الحفاز E-Cat/Z280 مما يدل على أن Z280 سهلت زيادة تكسير نوعية المركبات المتفاعلة في مدى الغازولين إلى أوليفينات خفيفة.

CHAPTER 1

INTRODUCTION

1.1 Background

Thermal cracking of various hydrocarbons is currently the main source of light olefins but intense research is ongoing to develop cost-effective catalytic routes that are less energy intensive and that emit less carbon emissions [1,28]. Propylene is one of the most important petrochemical industry feedstock. It is a very important starting material for the production of such important polymers as polypropylene [1,3]. The three major means of producing propylene industrially in order of importance are: steam cracking of light naphtha, Fluid Catalytic Cracking (FCC) of gas oils and propane dehydrogenation. They accounted for 60-65%, 30% and 5-10% of the entire propylene production in 2011 respectively [1]. Over the next decade, there is a predicted steady rise in the world demand for propylene, it is increasingly becoming more attractive than ethylene in the petrochemical industries [1,2]. Due to the projected increase in demand for propylene, many refiners are currently researching the viability of using non-conventional feeds such as crude oil and shale oil in FCC units directly [1,4].

In refineries, catalytic cracking is employed in the production of gasolines and light olefins. The conventional feeds used in the Fluid Catalytic Cracking (FCC) units of refineries are gas oils. The gas oil feedstock is obtained as a product from the fractional distillation of crude oil in a crude distillation unit, atmospheric tower or vacuum tower in a refinery [5,6]. There is increasing demand for light olefins, particularly propylene as

feedstocks in the petrochemical industries. This has led to attempts to directly crack whole crude oils in FCC units, bypassing the crude distillation units. Whole crude is crude oil as it is produced from a wellhead. It includes treatments such as desalting it may undergo to make it acceptable for conventional distillation in a refinery. Non-conventional oils such as shale oil are also termed as whole oil if used directly in cracking.

1.2 Fluid Catalytic Cracking (FCC)

In the FCC process, finely divided powdered catalyst is passed through a reactor as shown in Figure 1.1. The catalyst particles act as liquids and can be transported through pipes when aerated with air or hydrocarbon vapour. As the reaction proceeds, coke is deposited on the catalyst; hence the catalyst is continuously withdrawn from the bottom of the reactor to the regenerator for regeneration. In the regenerator, a controlled burning mechanism is used to burn off the coke [6].

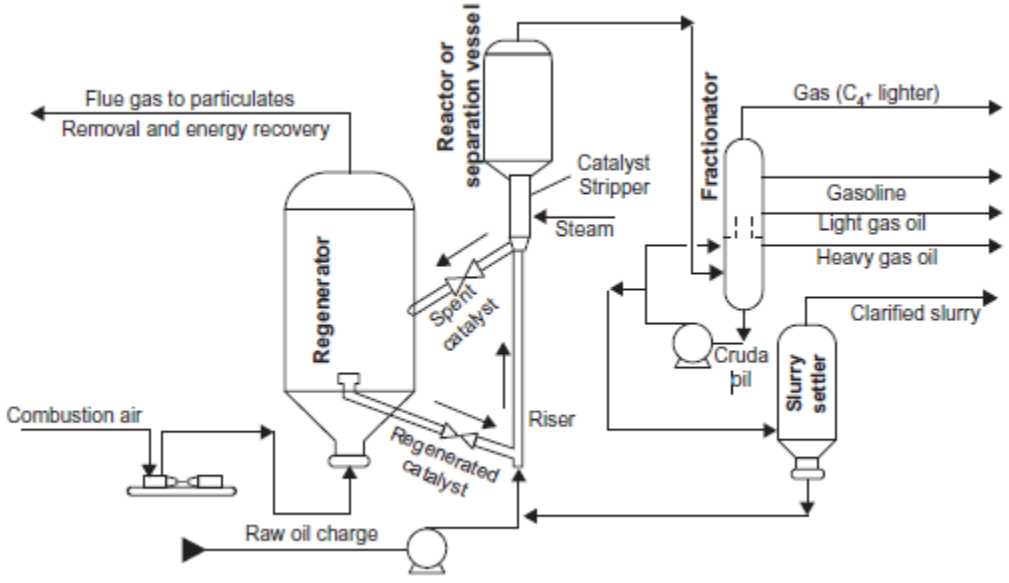

Figure 1.1 Schematic representation of an FCC reactor [6]

The hot regenerated catalyst is sent back to the fresh feed line where it vaporizes the fresh feed before it enters the reactor. In the FCC process, high temperatures (470°C to 565°C) are usually utilized to minimize coke deposits on the catalyst and reduce the secondary cracking of gasoline to lighter ends.

1.3 Fluid Catalytic Cracking (FCC) Catalysts and Light Olefins Boosting Additives

In general, FCC catalysts consist of two major components: zeolite and matrix. They may also contain a third component: one or several additives. These third components may be designed to boost gasoline octane, increase catalyst metal resistance, reduce SO, emissions, or facilitate CO oxidation [8]. The zeolites used in FCC catalysts are usually synthetic, faujasite type zeolites: Y and high-silica Y zeolites. Previously, X zeolites were used but they have been replaced by the more stable Y zeolites. Some commercial catalysts contain mixtures of Y and high-silica Y zeolites. Commercial FCC catalysts usually contain between 15 and 40% zeolite. The catalytic activity and selectivity of the FCC catalyst is usually dependent its zeolite content [8].

1.3.1 Factors to be considered in FCC catalysts design

Some of the important factors that influence the performance of fluid catalytic cracking catalysts are discussed below.

1. Feedstock: The feedstock greatly influences the design of the FCC catalyst used in the catalytic cracking process. A light paraffinic gas oil with is easier to crack than an aromatic feedstock. Feedstocks with high aromaticity require catalysts with higher

activity and low coke selectivity. Pre-treatment of the feedstock also has a significant impact on the design of the FCC catalyst. Hydrotreatment converts a heavily contaminated and difficult to crack feedstock into a lighter, contaminant free feedstock. This makes it easier to crack [8]

2. Process conditions: The process conditions in a FCC unit greatly affect the design of FCC catalysts. They are closely related to the other factors affecting the design of FCC catalysts. For instance when operations are designed to minimize dry gas and coke formation, catalysts with low dry gas and coke selectivities will be used. Also, the process parameters of that operation, such as C/O ratio, feed preheat temperature are optimized.

3. Product demands: This is another factor that affects the design of FCC catalysts. Catalysts containing rare earth exchanged Y zeolites, for instance, are more active and have better gasoline selectivities than those containing Y zeolites without rare earths. The catalyst matrix can be active or not. This depends upon the feedstock and the desired gasoline octane. Catalysts with high-activity matrix are being used if maximizing octane-barrels is the objective. So many other catalyst design configurations are possible depending on the desired product distribution [8].

Other factors to be considered in designing FCC catalysts include environmental considerations and overall catalyst cost [8].

1.3.2 FCC Additives

The most important Fluid Catalytic Cracking (FCC) additive for propylene production and gasoline octane improvement is ZSM-5 [14]. ZSM-5 is used in most of the FCC units

whose primary aim is to maximize propylene production. The action of the additive is to crack gasoline range additives into propylene and butylene mainly. Its pore size limitation leads to a shape selectivity that enhances the cracking of hydrocarbons with low octane numbers into light olefins [16]. The performance of ZSM-5 as a propylene boosting additive is also dependent on its acidity and mesoporosity. For VGO cracking, mesoporosity makes the active sites highly accessible [16]. ZSM-5 can also be used in combination with other additives to boost the light olefins yield of an FCC process [10,16].

1.4 Catalyst evaluation parameters

Three important parameters are used to explain the effect of catalysts on product yields. They are Hydrogen Transfer Coefficient, percentage increase in propylene yield per decrease in gasoline yield (%$C_3^=$/gasoline) and conversion. They are explained below.

1. Hydrogen Transfer Coefficient (HTC): This is defined as the ratio of butanes to butenes. It gives an indication of the tendency of the catalysts to undergo hydrogen transfer reactions [32]. Hydrogen transfer reactions consume light olefins (which are intermediate products in the catalytic cracking process) to form undesirable paraffins. Hence, for high light olefins production, low HTCs are required. HTC is a measure of hydrogen transfer activity of a catalyst with respect to feed composition. It is a bimolecular reaction that requires feed components to be in close proximity to a strong acid site [3]

2. Percentage increase in propylene yield per unit decrease in gasoline yield: This is the next parameter of importance. This is an important parameter because it shows the extent

at which propylene yield is increased at the expense of gasoline yield [35]. Industrially, the catalyst that produces a high amount of light olefins with a minimal decrease in gasoline yield, is preferred.

3. For our crude oil feeds, the conversion is defined as the percent of heavy ends (LCO+HCO+Bottoms) fraction in the crude oil cracked to gaseous and gasoline fractions. The heavy ends have a boiling range greater than 221°C. While for VGO, the conversion is 100-Gas Oil yield.

$$\text{Conversion}_{\text{Crude\_Oil}} = \frac{(LCO+HCO+Bottoms)in\ feed - (LCO+HCO+Bottoms)in\ product}{(LCO+HCO+Bottoms)in\ feed} * 100\% \quad (1.1)$$

$$\text{Conversion}_{\text{VGO}} = 100 - \text{Gas Oil Yield (wt.\%)} \quad (1.2)$$

1.5 Fluid Catalytic Cracking Feed

Commercially, the most common feeds used in FCC units are gas oils. These include atmospheric gas oils and vacuum gas oils. Resids are also used in FCC units, though they are less common. More recently, refiners have started blending whole crude oil (shale oil) with gas oils as feeds in FCC units.

1.5.1 Characterization of FCC Feed

The characterization of the feed characterization provides a means of relating feed quality to product yield and qualities. It is the process of determining physical and chemical properties of the feed. The types of hydrocarbon in the FCC feed are paraffins, olefins, naphthenes, and aromatics [1].

1. Paraffins: These are straight or branched chain hydrocarbon with the chemical formula C_nH_{2n+2}. Conventional FCC feeds are primarily paraffinic with a paraffin content of

between 50 %wt and 65 %wt of the total feed. They are easy to crack and produce the largest amounts of total liquid products and gasoline. They produce the least fuel gas and their gasoline fraction has the least octane number.

2. Olefins: These are unsaturated compounds. They have a chemical formula of C_nH_{2n}. Relative to paraffins they are unstable and can react with themselves or with other compounds. They do not occur naturally. They occur in the FCC feed as result of pre-processing the feeds in distillation units and catalytic cracking units. Whole crude oils do not contain olefins. They usually crack to form products such as slurry and coke hence they are undesirable feed components.

3. Naphthenes: Naphthenes are paraffins that have a ring or a cyclic shape. They have the chemical formula C_nH_{2n}. They are saturated compounds. Examples include cyclopentane and cyclohexane. They are desired as FCC feedstocks because they produce gasoline with high-octane number. Its gasoline has more aromatics and is heavier than the gasoline produced from the cracking of paraffins [8].

4. Aromatics: These are similar to naphthenes, but have a stabilized unsaturated ring core. They have the chemical formula C_nH_{2n-6}. They contain benzene which is very stable and does not crack to smaller components. They are not useful as FCC feedstocks since most of the molecules do not crack. The cracking of aromatics can result in excess fuel gas yield. Also, some of the aromatic compounds contain several rings that can compact and end up on the catalyst as carbon residue (coke) or slurry product. The cracking of aromatic stocks results in lower conversion, gasoline yield and less liquid volume gain with higher gasoline octane relative to paraffins [8].

1.5.2 FCC Feed Quality

The quality of FCC feedstock can be determined from its UOP K factor (K-factor). It ranges from 12.5 for very paraffinic feedstocks to 11.0 or less for aromatic feedstocks. The UOP Characterization Factor gives an idea of the general origin and nature of a petroleum stock. It is usually estimated from the API gravity of the FCC feed and distillation data.

1.6 Catalytic Cracking of Crude Oil

With the rise in availability of light unconventional crude oils such as shale oil, some refineries have begun charging crude oil or mixtures of crude oil and conventional FCC feeds directly into catalytic cracking units.

Processing of whole crude is necessary in refineries that have a high percentage of light crude because the refinery could become overloaded with light cuts and not enough heavy cut feed to be used in the FCC units [7]. In such a case the refineries shut down distillation units and feed the light crude oil directly into the FCC units to reduce shortage. Already, companies such as Exxon Mobil have developed steam crackers capable of cracking crude oil directly into petrochemicals instead of using conventional naphtha feed.

The catalytic cracking of light crude oil in FCC units has a particular disadvantage because it results in low coke. Coke is an important component for the heat balance of FCC units. Burning off coke from the spent catalyst is an endothermic process that provides the energy for heating the feed and catalyst for subsequent catalytic cracking [7]. A lot of gasoline is also produced from cracking light crude oil because there is a significant amount of gasoline fraction in the crude oil starting material. The gasoline

produced though, has low octane number. The LCO produced is of high quality (it has high diesel index) [7].

Fitzharris and his co-workers were issued a patent in 1989 for a new method for the catalytic cracking of whole crude oil. Their method was a success and also commercially viable. Basically, the process involves first desalting the crude oil followed by pre-heating it at 430 F. A flash drum was used to separate the vapors from the liquid portion and the flashed bottoms are sent to the Fluid Catalytic Cracking Unit (FCCU) [5]. A riser reactor was used for this process with reaction temperatures of 482 to 551ºC and crystalline aluminosilcates or zeolites used as catalysts. The products categories obtained from this novel method include: light hydrocarbons with boiling temperatures less than 221C, Light Catalytic Cycle Oil (LCCO) and Decanted Oil (DO).

The method developed by Fitzharris eliminated the need for the crude distillation units and as a result it was cost effective compared to the conventional FCC process in producing gasoline and light olefins. [5].

1.7 Thesis Objectives

The primary objective of the study is to investigate the suitability of using Arabian Whole Crude Oil as a feed in Fluid Catalytic Cracking Units to produce light olefins. The catalytic activity of commercial equilibrium catalysts and various zeolites additives used in the cracking will be evaluated at various temperatures.

The specific objectives are:

1. Maximizing Light Olefins yield from the Fluid Catalytic Cracking of Crude Oil for use in the petrochemical industries

2. Converting Saudi Crude into valuable products. The feeds to be used in the study are: Arabian Super Light Crude Oil, Arabian Extra Light Crude Oil and Arabian Light Crude Oil

3. Testing of different zeolite additives with the Equilibrium catalyst (E-cat) in the fluid catalytic cracking of whole crude. The additives (25 wt.%) are physically mixed with the E-cat (75 wt.%). The additives to be added to the catalyst are prepared by three methods namely: impregnating the additives with manganese by aqueous incipient wetness, by treatment of additives with alkali (desilication) and steam treatment.

4. Kinetic modelling using a Four –Lump model

1.8 Thesis Scope

Chapter 2 provides a background on fluid catalytic cracking (FCC) process, catalysts and additives. It also gives information on the whole crude oils, previous work on the catalytic cracking of gas oils and recent work on the catalytic cracking of non-conventional FCC feeds.

Chapter 3 gives an overview of the materials and feeds used in this work. It provides information on the various catalyst characterization methods used and also describes the additive modification process and the process for cracking crude oil in a microactivity test (MAT) unit.

In chapter 4, all the results are presented. First, the characterization results are presented. This is followed by the results obtained for the catalytic cracking of the three kinds of crude oil and a discussion of the trends obtained. Next, the product yields obtained from

the three crude oils are compared. A kinetic modelling of the experimental yields obtained on cracking the crude oils concludes this chapter.

Chapter 5 summarizes the findings of this thesis and gives recommendations for future works in the cracking of whole crude oil

CHAPTER 2

LITERATURE REVIEW

2.1 Background

This chapter provides a background on fluid catalytic cracking (FCC) process, catalytic cracking conditions, catalysts and additives. It also gives information on the whole crude oils, previous work on the catalytic cracking of gas oils and recent work on the catalytic cracking of non-conventional FCC feeds.

2.2 Fluid Catalytic Cracking (FCC) Catalysts

Commercially, FCC catalysts are classified as: octane boosting catalysts, resid catalysts and gasoline FCC catalyst. Each of the catalyst is named either by the desired end product composition or feedstock composition. Each of them uses varying types of FCC additives for their desired purposes [8]. Some of the factors to be taken into consideration in designing a Fluid Catalytic Cracking (FCC) catalyst are feedstock composition, reaction conditions and desired composition of products, FCC unit design and economics among others [8]. Treatments of an FCC feedstock are usually a determinant of the catalyst composition and properties utilized for its cracking [8].

Physical properties of importance in the design of FCC catalysts include particle and pore size distribution, thermal and hydrothermal stability, attrition resistance, bulk density and surface area. The catalytic performance of FCC catalysts is to a large extent, dependent on some of these physical properties [8]. Zeolites and matrix are the two major compositions of an FCC catalyst. Additives are added as the third catalyst component

depending on the desired product distribution. Synthetic, faujasite type zeolites (Y and high-silica Y zeolites) are the major kinds of zeolites in use for manufacturing FCC catalysts [8,9]. Commercial FCC catalysts contain about 15-40% zeolite content. The catalyst matrix consists of a synthetic and a natural component.

Matrices, which have a natural and synthetic component, give the FCC catalyst its representative physical properties but may also have some catalytic impact. Clay is the most widely used natural component and silica/alumina usually makes up the synthetic portion of the matrix of FCC catalysts [8]. Zeolite/Matrix ratio of an FCC catalyst has a great impact on the product yields. Scherzer [8] showed that C_3/C_4 product yield decreased from a value of 15 wt% to around 12 wt% as the zeolite/matrix increased from 0 to 4 while the reverse was observed for the product gasoline content. The compositions of a typical FCC catalyst are shown in Figure 2.1

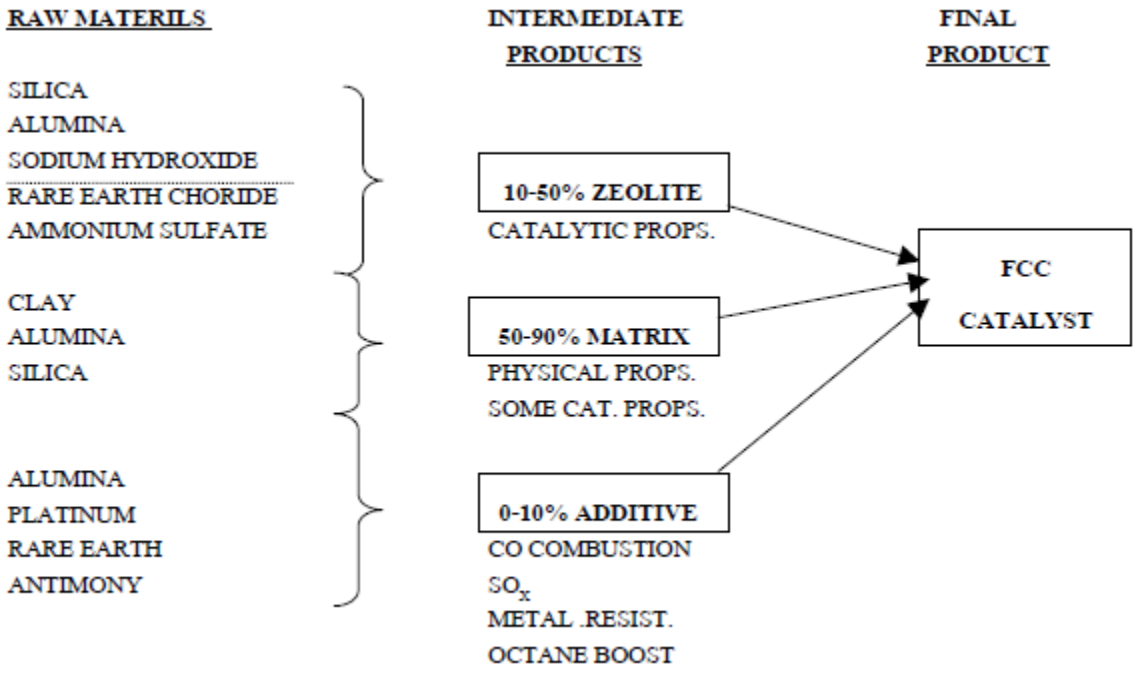

Figure 2.1 Composition of a typical FCC catalyst

For maximizing propylene yield, FCC catalysts must have high activity, must be stable and produce amounts of coke. In some instances, there has to be a trade-off between stability of the catalyst and low hydrogen transfer for greater propylene yield [10].

The pore structure of the catalyst ranges from micropores, mesopores to micropores with each having a specific role in the cracking process. For the cracking of heavy molecules into valuable gasoline and gas oil products, the micropores and mesopores are the most catalytically important [11-13].

FCC catalysts ensure high propylene yield because they have rapid cracking activity which ensures the feed is cracked before unwanted thermal cracking sets in. Also, they have excellent hydrothermal stability, relatively large pore sizes for efficient cracking of large molecules, reduced coke production to lessen the deactivation of the catalyst and excellent attrition resistance [1]. Hydrogen transfer, oligomerization, isomerization and aromatization are some of the reactions that need to be limited for the purpose of increased propylene selectivity and olefinicity of the gasoline.

2.2.1 Hydrogen Transfer

Hydrogen transfer reactions are very important in determining product selectivities of modern cracking catalysts. The reaction between olefins and naphthenes yields paraffins and aromatic as products. Naphthenes are a major constituent of most FCC feeds hence olefin from the primary cracking reactions is all that is required to initiate hydrogen transfer reactions. For instance, butene can react with cyclohexane to make butane and benzene**.** A valuable light olefin is used up to make a light gas and an aromatic. This product is not particularly desirable [1]. Hydrogen transfer reactions occur readily in type Y zeolite catalysts. Hydrogen transfer also enhances the formation of condensed aromatic

rings that lead to increased coke formation and a reduction of olefins in the product. Also, the molecular weight distribution of the products is increased by hydrogen transfer because the carbenium ions are converted to paraffins which is undesirable.

Modification of the catalyst's zeolite structure helps to control hydrogen transfer reactions. Reduced hydrogen transfer results in lower gasoline yields, low coke yield, and high olefin yield. Increased olefins yield, isoparaffins and aromatics help enhance gasoline octane [8].

2.2.2 Mechanism of Catalytic Cracking

The two major mechanisms of the cracking of hydrocarbon over zeolites are given below:

1. Monomolecular mechanism (protolytic cracking): It is the dominant mechanism in medium pore shape selective zeolites. It allows for the formation of large quantities of ethylene and propylene [28]. In this mechanism, alkanes are protonated to form carbonium ion transition states. Then the carbonium ion undergoes either C-C bond cleavage (to produce alkanes) or C-H bond cleavage (to produce hydrogen and carbenium ions). The carbenium ions form alkanes by back donation of a proton to the zeolite

2. Bimolecular mechanism: In this mechanism, branched secondary and tertiary alkyl carbenium ions are obtained from the feed molecules. They are then cleaved by a single beta-scission into smaller alkyl carbenium ions and alkanes.

2.3 Fluid Catalytic Cracking Additives

Additives added to FCC catalysts (in the refineries or by the catalyst manufacturers) may contribute to catalytic activity or may be present for other purposes such as reduction of pollutants. They are added to compensate for allowances that were made in the FCC

parent catalyst design [10]. Good additives should be highly stable and have physical properties which mirror those of the parent catalyst as well as having good cracking activity [8]. Some of the categories of additives in use industrially include:

(i) Octane boosting additives and light olefins boosting additives such as ZSM-5

(ii) SOx reducing additives such as inorganic oxides and mixed oxides

(iii) Carbon (II) oxide combustion promoters such as Pt and Si/Al

(iv) Metal traps such as metal oxides and natural clays [8]

Commercially, the single most important Fluid Catalytic Cracking additive for propylene production and gasoline octane improvement is ZSM-5 [14]. ZSM-5 is used in most of the FCC units whose primary aim is to maximize propylene production. Utilizing FCC catalysts alone without ZSM-5 additives could have considerable detrimental effects on the yields of coke and gas, all without a great increase in the propylene product [15].

Also, increasing conversion of the equilibrium catalyst (E-Cat) used and the E-cat/Additives led to a corresponding increase in the yield of the ethylene, propylene and butylene [10,16].

2.4 ZSM-5 as an additive for Enhanced Propylene Production

ZSM-5 has a pore size limitation that leads to a shape selectivity that enhances the cracking of hydrocarbons with low octane numbers into light olefins [16]. The action of the additive is to crack gasoline range additives into propylene and butylene mainly. Figure 2.2 shows the effect of ZSM-5 in cracking gasoline to boost light olefins yield. The performance of ZSM-5 as a propylene boosting additive is also dependent on its

acidity and mesoporosity. For VGO cracking, mesoporosity makes the active sites highly accessible [16].

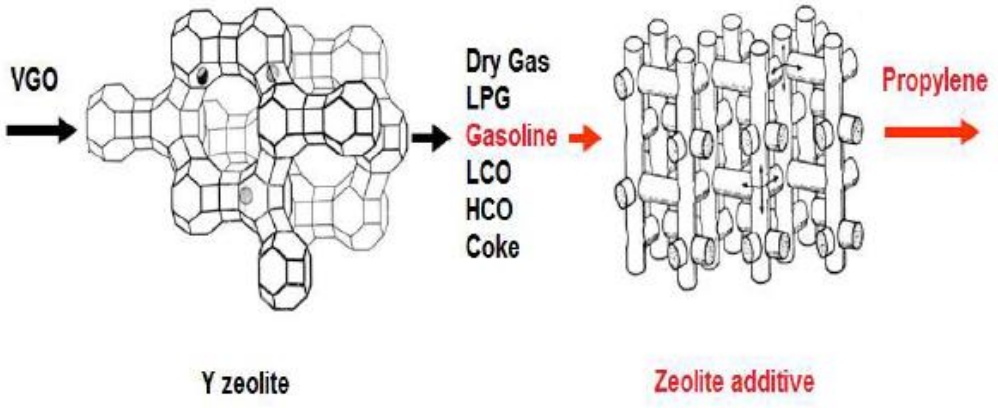

Figure 2.2 Effect of E-Cat and zeolite additive in increasing propylene yield

Various studies have been carried out to determine the effect of using ZSM-5 in combination with other additives to boost the light olefins yield of an FCC process. Jermy et al [10,16] in 2012 studied the effect of using a combination of ZSM-5 and MCM-41(ZM13) additives in the cracking of Arabian Light Hydrotreated VGO to increase the yield of propylene. In comparing the yield obtained from the ZM13 additives with conventional ZSM-5 additives at a constant amount of gasoline yield lost, they achieved propylene yield of 12.2wt% for the former additive and 8.6wt% for the latter, showing a superiority of ZM13 over ZSM-5 in boosting propylene yield. Also, increasing conversion of the equilibrium catalyst (E-Cat) used and the E-cat/Additives led to a corresponding increase in the yield of the ethylene, propylene and butylene [10,16]. Commercially, ZSM-5 can be added to E-Cats at high percentages of 25-30% [16]. When

the amount of ZSM-5 added to a base catalyst is greater than about 10%, there could be a dilution effect problem, if the aim is to increase propylene yield [10]. Some propriety catalysts such as Super Z and Propyl Max with high ZSM-5 content have been developed to tackle this problem [10]. ZSM-5 as an additive offers the advantage that it selectively promotes some reactions and the octane and light olefins boost is achieved with no parallel increase in the unwanted coke and C_2 [10].

When used in catalytic cracking, ZSM-5 works by cracking the olefins in the feed before they form paraffins via their reaction with hydrogen, hence they can be used even with the presence of copious amounts of Re_2O_3 in the FCC catalyst [10].For greater propylene yield, the activity of the ZSM-5 is of utmost importance and recent efforts have been made to increase this by developments in the technology used in the binders to make the zeolites more stable and accessible, simultaneously leading to higher activity per zeolite unit [10].

ZSM-5 can be used synergistically with other additives for greater effect. Many of these co-additives have been tested and are available commercially. Examples include bottom cracking additives (BCA-110 Plus) and high activity ZSM-5 (Super Z) which when added together have been shown to give greater propylene yield and increased conversion [10].

Feed metals content particularly Vanadium can have a profound effect on the quality of product yields. At low vanadium content, the Y-zeolite and ZSM-5 additive get deactivated at practically the same rate and the product yield and quality are optimum. But when the vanadium content is high, greater than 2000ppm, Y-zeolite activity loss

proceeds at a much faster rate than the ZSM-5 activity loss, leading to quality of product yield which are not optimal [10].

Vanadium doesn't greatly affect ZSM-5 additive activity probably as a result of ZSM-5's widely siliceous composition. ZSM-5 has a prolonged activity relative to a base catalyst because coke deposits on it less rapidly than on Y-zeolite [14].

Phosphorus when added as a stabilizer to ZSM-5 has great benefits on its shape selectivity and stability. It prevents Al from being extracted from the framework of the zeolite. In the long run it produces a zeolite which keeps a larger percentage of its initial acidity. Degnan et al reported that the greater retention of aluminium in the zeolite network of ZSM-5 is responsible for the stabilization of its cracking activity [14]. Additives in which the ZSM-5 content is high generally produce copious amounts of desirable light olefins, and have the added advantage of not over-diluting the base catalyst [14].

2.4.1 Effect of ZSM-5 amount used with a base catalyst

Increase in propylene yield as a result of ZSM-5 additives levels off when the ZSM-5 concentration is around 10wt% or higher. At ZSM-5 concentration level of about 10 wt.%, most of the gasoline-range olefins have already been converted to lighter ends, further increase in ZSM-5 amount leads to minimal conversion. Bulatov and Jirnov [17] studied the effect of varying concentration of ZSM-5 additives on FCC catalyst. Using a constant catalyst/oil ratio of 28, they determined that on increasing the ZSM-5 content from 0 to 10% by weight, the propylene yield correspondingly increased from 16wt% to 20wt%. Further increase of the ZSM-5 content of the FCC catalyst from 10wt% to 40% merely resulted in approximately 2% increase in the propylene yield [17]. This is because

the action of ZSM-5 in increasing propylene yield is to selectively crack the olefins in the gasoline range; the more the amount of ZSM-5 present, the lower will be the increased yield of propylene per amount of ZSM-5 additive used [1].

2.4.2 Effect of ZSM-5 crystal size on FCC catalyst activity

The rate limiting step in the catalytic reactions where large molecules is involved is the diffusion of molecules to the internal surface of the catalyst. A reduction in the particle size of the catalyst helps to alleviate this diffusion process since the diffusional path length is considerably reduced [18]. Using macro sized ZSM-5 and nano-sized ZSM-5 in the cracking of n-Hexane, Konno et al showed that the nano ZSM-5 achieved higher conversion and greater stability than the macro-zeolite. This is because for the nano-ZSM-5, pore diffusion wasn't rate limiting as a result of its reduced size and as a consequence, the blockage of pores due to deposition of coke was reduced [19].

Decreasing the size of the zeolite crystal is advantageous for propylene production because there is an improvement in intra crystalline diffusion[20]. Gao et al investigated this trend using two ZSM-5 catalysts with average sizes of 5.48μm (normal ZSM-5) and 1.99 μm (small particle ZSM-5) in the catalytic cracking of Xinjiang Vacuum Tower Bottoms (VTB), Xinjiang VGO and a mixture of VTB and VGO (VTB:VGO = 3:7). The reaction temperature used was 535ºC with a constant C/O ratio of 5.0 [20].

The two ZSM-5 additives had similar crystallinity which showed that save for the particle size, the physicochemical properties of the two ZSM-5s were similar and they were stable. Using a MAT unit, it was observed that the conversion for both were almost the same. For all the feeds, the smaller ZSM-5 additive generated more propylene because of

its more accessible acid sites [20]. It was also shown that the attrite index with a decrease in the particle size.

2.4.3 Effect of Si/Al ratio of ZSM-5 on catalyst activity

The effect of altering the Si/Al ratio of the ZSM-5 present in FCC catalyst is a corresponding change in the cracking/isomerization ratio [1]. Non-selective catalysis has been shown by Paparatto et al [21] to occur on the pore mouths and external surface of zeolites. Hydrogen transfer reactions, which are undesirable for enhanced propylene yield, occur on the external surface of ZSM-5 particularly at low Si/Al ratio and high levels of acidity. A zeolite with small crystal size and high Si/Al ratio ensures high propylene yield because of the faster elution of the primary products from the catalyst pores [22].

High Si/Al ratio also translates to lower zeolite acidity, meaning reduced overall reduction in the amount of coke deposited as a result of lower hydrogen transfer reactions. This leads to greater stability of the catalyst [1].

2.4.4 Effect of ZSM-5 on the formation of coke

Various forms of coke can be formed during a heterogeneous catalysed reaction such as fluid catalytic cracking. These are thermal coke, catalytic coke, C/O coke, contaminant coke additive coke and catalytic coke, all of which have varying formation mechanisms [1]. Factors affecting coke formation when zeolites are used include the pore size, pore structure and acidity of the zeolite. In particular, ZSM-5 forms low levels of coke relative to zeolite Y because its pores are narrow, reducing the amount of bulky coke intermediates formed [23].

2.5 Effect of reaction variables on propylene yield

Fluid catalytic cracking reaction variables, along with catalysts employed and the reactor used, determine the product yield and selectivity.

2.5.1 Effect of temperature

Using Daqing Atmospheric feed and CEP-1 catalyst, Meng et al [24] showed the relationship between temperature and product yields in Fluid catalytic cracking. At a constant catalyst/oil ratio and a temperature range of 600ºC - 716ºC, they observed the following trends in product yield. On increasing the reaction temperature, propylene yield increased up to a temperature of around 640ºC (optimal reaction temperature) and decreased subsequently as the temperature was further increased. Ethylene and dry gas yields on the other hand showed a positive linear relationship with temperature; they increased as the reaction temperature increased [24]. Propylene and butylene yields decreased at high temperatures because at such temperatures, being intermediates, they can undergo further secondary reactions which include the undesirable hydrogen transfer reactions, thus depleting their amount [1].

2.5.2 Effect of C/O ratio

Increase in the catalyst/oil ratio of an FCC reaction leads to a higher conversion, but this does not invariably result in increased propylene yield. In their work, Meng et al [24] showed that increasing C/O ratio leads to an initial increase in light olefins yield up to a maximum, followed by a decrease in its yield. Dry gas, coke make and conversion all increased with increasing C/O ratio. Increasing C/O results in increased temperatures for

equivalent conversions and this leads to the same effect as previously showed by Meng et al [24].

2.5.3 Effect of feed quality

The feed constituent which has a direct consequence on the conversion of the feed is aromatics. Aromatics have low levels of hydrogen and this makes resistant to cracking while also reducing the amount propylene that can be potentially formed, since propylene production requires hydrogen. Also important is the amount of Conradson Carbon (dependent on the amount of heavy molecules present in the feed) present on the feed. This Conradson carbon ultimately forms coke during the reaction which is detrimental to the production of yield [1].

With for different FCC feeds, at a constant temperature of 660ºC and constant C/O, Meng et al [24] showed that the propylene, butylene and total light olefins yields decreased with increasing aromatics content of the FCC feeds. The selectivity also decreased with increasing feed aromatic content [24].

2.6 Novel Zeolites additives for enhanced propylene production

TNU-9 (medium pore), SSZ-33 (large pore) Meso-Z and ZSM-5 (mesoporous) were investigated for use as FCC catalyst additives in the FCC of Arabian Light Vacuum Gas Oil by Siddiqui et [3] for enhanced propylene production. They observed a linear relationship between the conversion and C/O ratio while the conversion increased with increasing pore dimensions and total acidity. Meso-Z yielded the highest amount of light olefins because it showed the least Hydrogen Transfer Coefficient (HTC). HTC is the ratio of butanes to butenes product yield; low HTC can be attributed to great zeolite pore

structure accessibility, low zeolite acidity and swift removal of the primary products formed due to presence of mesopores in the zeolite [3]. Utilizing ZSM-5/MCM-41 composite as additives in the FCC with a Catalyst: Additives ratio of 9:1 wt%, Jermy et al [16] obtained similar results to the above.

2.7 Catalyst Additive Modification Techniques

Usually, for enhanced product selectivities, additives are modified in various which include desilication, metal impregnation and steaming.

2.7.1 Desilication

Desilication is the selective extraction of framework silicon by treatment in alkaline solutions. Small zeolite catalysts impose diffusion limitations under FCC conditions. Introduction of large pores into the zeolite crystals eases the diffusion limitation by allowing larger hydrocarbon molecules in the feed to diffuse to the crystals and get cracked into desirable products. Desilication induces intracrystalline mesopores, which are cracks, cavities and cylindrical channels in the crystals in the mesopores range that are connected in a wormhole-like manner to each other [25]. NaoH, KOH and LiOH are usually utilized in the desilication of ZSM-5 [26]. Introduced mesoporosity also leads to more gasoline, LCO and LPG because they diffuse faster before the formation of coke and dry gases by over cracking [27]. The process of desilication of zeolites is given as:

First is the ion exchange of NH_4^+ or H^+ in the starting zeolite with excess Na^+, K^+, Li^+ in the alkaline solutions. This is followed by additional ion-exchange with NH_4NO_3 and finally the zeolite is calcined to have it in the proton form.

Strong organic bases could also be used as the desilicating agents. They require more time and higher temperature than NaOH but they give precise control of the developed mesopores and also directly produce zeolite in the protonic form making its ion exchange easier [26].

2.7.2 Element Modification of zeolite additives

Bronsted acid centres are usually the catalytically active sites of H-zeolites. Introduction of metals such as alkali earth metals lead to the transformation of strong acid sites into weak ones. Bronsted acid site signal decreases with increasing degree of ion exchange. Additions of Fe and Phosphorus to the zeolites also lead to increased light olefins production because of the increase in oligomerization and cyclization reactions. Both metals decrease the Bronsted acidity and weaken strong Bronsted acid sites, which together enhances light olefins production. Anti-coking ability is also enhanced [28].

2.8 Fluid Catalytic Cracking of Whole Crude Oil

In this section, the concept of whole crude oil is introduced. Also, recent work in the fluid catalytic cracking of whole crude oils is discussed.

2.8.1 Whole Crude Oil

Whole Crude Oil is crude oil is crude oil as it is produced from the wellheads and has undergone pre-treatment such as desalting. It is the feed used in the crude distillation units of refineries. Crude oil is a readily available feed source which can help meet increasing demand for light olefins. It eliminates the need to use Crude Distillation Units hence, it is cost effective. Table 2.1 lists the boiling range of the various crude oil fractions as obtained from simulated distillation.

Table 2.1 Crude Oil Boiling Fractions

Boiling Range	Name
0-35°C	Light Ends
36-221°C	Gasoline
222-343°C	Light Cycle Oil (LCO)
344-540°C	Heavy Cycle Oil (HCO)
>541°C	Bottoms

It is estimated that by 2035, 7% of the total global oil supply will be obtained from Tight Oils which includes Shale oil, hence the push to fully understand how to respond under conventional refinery conditions and processes. Challenges faced in processing these kinds of crude in the refinery include non-specific heat balances and large amount of metal contaminants [7]. Using a feed of whole Bakken Crude, Bryden et al [7] investigated the possibility of using shale oil as feed directly in conventional fluid catalytic cracking processes. The crude has an API of 42º, sulphur content of 0.19% and FCC feed of lower than 28%. A commercial zeolite catalyst with a surface area of 196m^2/g was used with a C/O ratio of 6, a high conversion of 83.5wt% was obtained at 980 ºF in an ACE unit. Here, conversion was defined as 100 - (LCO wt%+Bottoms wt %).

The amount of bottoms in the product was little, so also was the coke yield. At a constant conversion, a decrease in the reaction temperature results in slightly more gasoline yield. At 970 ºF, relative to a Mid-Continent VGO feed used, more gasoline, less LCO and less coke were obtained. The gasoline obtained from this cracking was paraffinic and of low quality. It has RON < 80 and MON < 70 [7].

CHAPTER 3

MATERIALS AND METHODS

3.1 Background

This chapter gives an overview of the materials and feeds used in this work. It provides information on the various catalyst characterization methods used and also describes the additive modification process and the process for cracking crude oil in a microactivity test (MAT) unit.

3.2 Feed

The crude oil feeds used in this study; Arabian light (ASL), Arabian extra light (AXL) and Arabian Light (AL) were procured from a domestic refinery. The properties of ASL, AXL, AL and VGO are listed in Table 3.1. ASL feed is a low-sulfur crude oil with an API gravity of 51^{o}, AXL has an API of 39^{o} and higher sulfur content was about 1.2 wt.% while AL has an API gravity of 34° and the highest sulphur content of 1.8 wt.%. Simulated distillation results showed that the content of 221 °C+ fraction (middle distillate and heavier hydrocarbons) in ASL, AXL, AL and VGO feeds was 56.0, 67.0, 69.0 and 100 wt.%, respectively. The gasoline fraction (C_5-221°C) in ASL, AXL and AL crude oils was 44, 34 and 31 wt.% respectively. Based on PIONA analysis, the composition of gasoline fractions of the three crude oils was highly paraffinic (~65 wt.%) while aromatic content was 15 wt% in ASL and 27 wt.% in both AXL and AL. Naphthenes were 8 % in AXL and AL compared with 19 % in ASL. The GC-RON was 53 for ASL, 48 for AXL and 61 for AL.

3.3 Base Catalyst

The base catalyst was a commercial equilibrium FCC catalyst (E-cat) received from a domestic refinery. It has a BET surface area of 135 m^2/g, and pore volume of 0.23 cc/g. Other textural properties of the base E-cat are given in Table 3.2. The E-cat was calcined at 550^{o}C for three hours prior to its use. The temperature was increased at 5^{o}C/min during calcination.

3.4 Additives

ZSM-5 zeolites are well known additives for olefins enhancement from VGO cracking. To investigate the effect of the ZSM-5 on the light olefins enhancement from crude oil cracking, three ZSM-5 zeolites of varying Si/Al molar ratio (Z-30, Z-280, Z-1500) were used. Modified forms of Z-280 were also used as additives (Table 3.3). Z-280 was modified by steaming (St-Z-280), alkali-treatment DS-Z-280) and metal impregnation (Mn-Z-280). Mn was used, as it was shown to enhance the light olefins yields from VGO cracking. The prior modifications were done to create mesoporosity, which increases the light olefins yields from the cracking of hydrocarbons.

Table 3.1 Physical Properties of Arabian Super Light (ASL), Arabian Extra Light (AXL) and Arabian Light (AL) crude oil feeds

Property	ASL	AXL	AL	VGO
Gravity, °API	51	39	34	27
Density at 15°C, kg/m^3	774	828	892	894
Sulfur (wt.%)	0.02	0.81	1.77	0.03
Vanadium (ppm)	1	1.1	16	-
Nickel (ppm)	< 1	< 1	3.3	-
Nitrogen (ppm)	44	434	-	-
Hydrocarbon Types				
Saturates (wt.%)	12	14	12	-
Aromatics (wt.%)	50	58	57	-
Polars	27	27	28	-
Asphaltene	1	1.2	3	-
Microcarbon Residue (wt.%)	0.46	2.20	3.6	-
Kin. Viscosity, @ 20 °C (cSt)	1.8	4.8	10.2	-
Elemental analysis, %				
C	85	84	84	87
H	14	13	13	12
N	0.53	0.70	.64	-
Gasoline GC-RON	53	48	61	
Gasoline composition, wt.%				
iso-paraffins	35	34	47	-
n-paraffins	32	31	18	-
naphthenes	19	9	9	-
aromatics	15	27	27	-
Simulated Distillation (°C)				
Initial boiling point	22	25	22	308
5%	71	85	87	
25%	157	185	196	
50%	242	287	307	420
90%	435	491	507	
Final boiling point	558	577	580	568
Light ends (0-35^{o}C)	2	2	2	-
Gasoline (35-221^{o}C)	42	32	29	-
LCO (221-343^{o}C)	30	28	27	1
HCO (34-540^{o}C)	26	35	37	99
Bottoms (540^o C+)	-	3	5	-

Table 3.2 Properties of commercial equilibrium USY based FCC catalyst

Property	Units
BET surface area	*135 m^2/g*
Mesoporous surface area	*31.1 m^2/g*
Pore volume	*0.23 cc/g*
SiO_2	*54.1 wt.%*
Al_2O_3	*40.7 wt.%*
Rare earth	*2.0 wt.%*
Ni	*trace*
V	*trace*

Table 3.3 List of reference and modified additives

S. No	Additive	Description
1	Z-30	Zeolyst CBV3024, ZSM-5 (Si/Al_2=30)
2	Z-280	Zeolyst CBV28014, ZSM-5 (Si/Al_2=280)
3	Z-1500	Tosoh, Japan, (Si/Al_2=1500)
4	St-Z-280	Steamed Z-280
5	DS-Z-280	Alkali-treated Z-280
6	Mn-280	2%Mn impregnated Z-280

The ZSM-5 zeolites (Z-30, Z-280 and Z-1500) were procured from Zeolyst International. These zeolites were in ammonium form and were calcined at 550^{o}C for 3 hours before use. The modifications on Z-280 were done as described below:

St-Z-280: It was prepared by steaming Z-280 in a fixed-bed steamer. The sample was heated slowly at 5^o/min up to 600^{o}C in nitrogen flow. Steam flow was started at 600^{o}C and steaming was carried out for 6 hours.

DS-Z-280: was prepared by desilication of Z-280. Desilication was done using 0.1M sodium hydroxide (NaOH) solution at 60°C for 2 h, under atmospheric pressure. Typically, 300 ml of the 0.1M NaOH solution was heated up to 60 °C in a round bottom flask fitted with a reflux, and then 5 g of the zeolite was added. After 2 h of continuous stirring, the mixture was cooled using ice bath and filtered. The obtained product was washed using deionized water and then dried at room temperature, followed by overnight drying at 100 °C. The desilicated sample was ion-exchanged using 1.0M of ammonium chloride at 70 °C for 5 h (3 times). The sample was calcined in air at 550 °C for 6 h.

Mn-Z-280 was prepared using incipient wetness impregnation method. In a typical synthesis, appropriate amount of manganese (II) nitrate hexahydrate corresponding to 2.0 wt% of Mn loading was dissolved in deionized water. The obtained solution was mixed with Z-280 powder and the slurry was dried in an oven at 100°C for overnight. The obtained solid was calcined in air at 550 °C for 6 h.

3.4.1 E-cat/additives catalyst preparation

The calcined additives were pelletized, crushed and 80-90 μ size of the material was sieved out. Catalysts for testing were prepared by mixing and physically blending 75 wt.% of E-cat and 25 wt.% of sieved additives. It is reported that the maximum enhancement in light olefins yield occurs at 25 wt.% of additive level [35]. Above 25 wt. % of additive level in the E-cat/additive blend, significant decrease in the conversion was observed due to dilution effect.

3.5 Catalyst Characterization

The crystallinity of the zeolites used in this study was determimed by X-ray powder diffraction (XRD) using a Rikagu Miniflex desktop diffractometer with a graphite monochromator.

The textural properties of the zeolite additives were determined by N_2 adsorption measurements at 77K, using Micromeritics ASAP 2020 analyzer. Samples were out-gassed at 350^oC under 10^{-5} torr vacuum for 3 h before adsorption measurements. The BET surface area were calculated from the desorption data in the relative pressure (P/Po) range of 0.06 to 0.2.

The shape of the zeolite crystals were determined by scanning electron microscopy (Jeol, JSM-5500LV). Temperature programmed desorption (TPD) technique was used to measure the acidic properties. The TPD measurement was carried out using Mettler Toledo Star instrument.

3.6 Evaluation of Catalysts/additives

The crude oil feeds, ASL, AXL and AL, were cracked in a fixed-bed microactivity test (MAT) unit using E-cat, to assess their crackability in a Fluid Catalytic Cracking Unit (FCCU). The MAT unit is shown in Figure 3.1. To examine the impact of crude oil cracking on the FCC product yields especially that of light olefins yields, cracking tests were done using E-cat and additive blends.

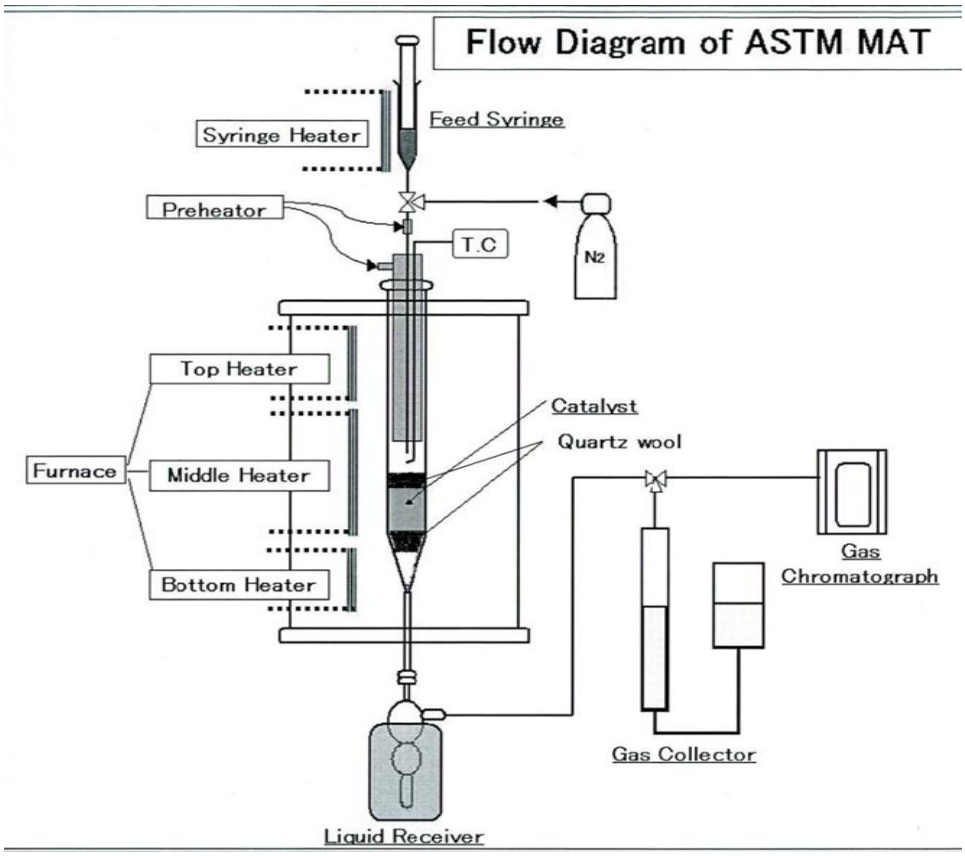

Figure 3.1: Flow diagram of a microactivity test (MAT) unit

The MAT tests were performed as per the standard ASTM D-3907 method. The feed injection system was modified to inject heavy crude oil feeds. The MAT runs were conducted in a temperature range of 475^{o}C and 550^{o}C and 30 s of time-on-stream. Conversion was varied by changing the catalyst/oil (C/O) ratio in the range of 1-4 g/g by changing the quantity of catalyst and keeping constant the amount (1.0 g) of crude oil feed.

MAT product comprises of gases, liquid, and coke. Gaseous products were analyzed using an Agilent 3000A MicroGC. This analyzer consists of a multi-channel and multi-column system equipped with four thermal conductivity detectors (TCD). All the light

hydrocarbons up to C_4, C_5 paraffin, hydrogen, and fixed gases were quantitatively analyzed in one injection. The GC was calibrated with standard gas mixture. Liquid product was analyzed by simulated distillation method (ASTM D-2887) using Shimadzu GC 2010 Plus equipped with a Flame Ionization Detector (FID).

Coke on the spent catalyst was determined using a Horiba Carbon-Sulfur Analyzer Model EMIA-220V. About one gram of the spent catalyst (with tungsten added as combustion promoters) was burnt in the high temperature furnace. The resulting combustion gas (CO_2) was passed through an Infra-Red Analyzer and the carbon content was calculated as a percent of the catalyst weight.

The above three analytical results were combined to obtain the detailed product yield patterns and information on the cracking ability of crude oils and on the selectivity of the additives being investigated.

For our crude oil feeds, the conversion is defined as the percent of heavy ends (LCO+HCO+Bottoms) fraction in the crude oil cracked to gaseous and gasoline fractions. The heavy ends have a boiling range greater than 221°C. While for VGO, the conversion is 100-Gas Oil yield.

$$\text{Conversion}_{\text{Crude\_Oil}} = \frac{(LCO+HCO+Bottoms)in\ feed - (LCO+HCO+Bottoms)in\ product}{(LCO+HCO+Bottoms)in\ feed} * 100\% \quad (3.1)$$

$$\text{Conversion}_{\text{VGO}} = 100 - \text{Gas Oil Yield (wt.\%)} \quad (3.2)$$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Background

In this chapter, all the results are presented. First, the characterization results are presented and discussed. This is followed by the results obtained for the catalytic cracking of the three kinds of crude oil and a discussion of the trends obtained. Next, the product yields obtained from the three crude oils are compared. A kinetic modelling of the experimental yields obtained on cracking the crude oils concludes this chapter.

4.2 Catalyst characterization

XRD patterns of the zeolite additives under investigation in this study are shown in Figure 4.1. All the additives show characteristic peaks of ZSM-5 between 8-9° and 22-25° [29]. However, the intensity of peak at 22-25° decreased for DS-Z-280 additive showing a slight decrease in crystallinity, but there was no change in crystallinity of other additives.

The nitrogen adsorption isotherms of the zeolite additives shown in Figure 4.2 exhibit type I isotherm, typical of microporous materials. The increase in the adsorbed amount between p/p_0 of 0.9 and 1.0 is due to the adsorption in interparticle voids [30]. The BET surface area increased from $333 m^2/g$ (Z30) to $370\ m^2/g$ (Z280) and then reduced to $335 m^2/g$ (Z1500) as shown in Table 4.1. Steamed Z280 additive displayed reduced BET surface area which is as a result of dealumination leading to loss of surface area.

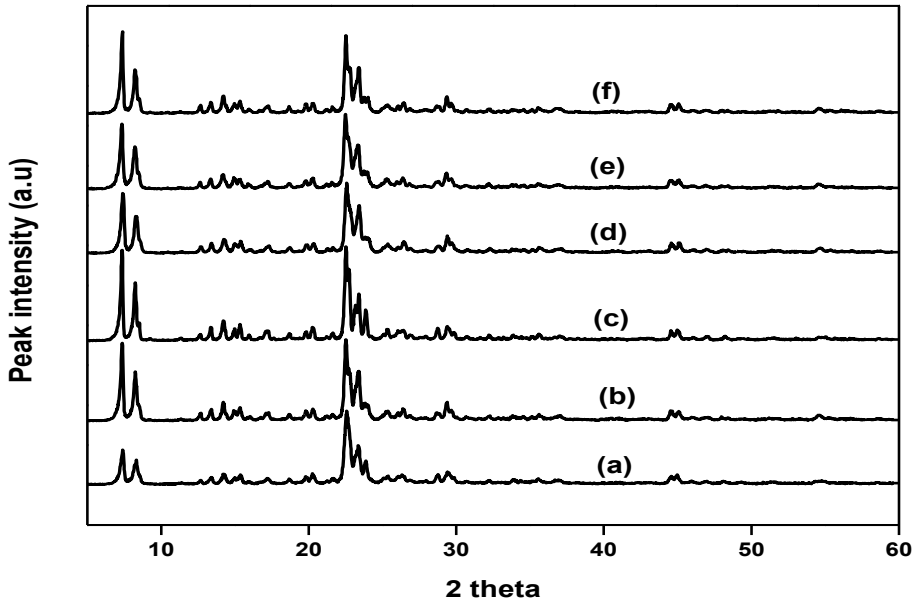

Figure 4.1 XRD patterns of (a) Z-30 (b) Z-280 (c) Z-1500 (d) St-Z-280 (e) DS-Z-280 (f) Mn-Z-280

The t-plot method was used to determine the micropore volume of the additives. Z280 has the lowest micropore volume (0.05cc/g) but highest mesopore volume (0.15cc/g). The micropore volume of St.Z280 didn't show much change as a result of steam treatment but there was a decrease in mesopores volume from 0.15cc/g to 0.11cc/g which indicates a loss in mesoporosity due to steaming.

TPD of ammonia results for all additive samples are shown in Figure 4.3. Two peaks corresponding to weak (100-300 °C) and medium (300-450 °C) acid sites were identified. The intensities of both weak and medium acid sites were observed to increase with decrease in Si/Al ratio of ZSM-5 additives. The total acidity of the zeolite decreased with increasing Si/Al molar ratio as shown in Table 4.1. This is because of the relative loss in the number of Al atoms responsible for the zeolites' acid sites.

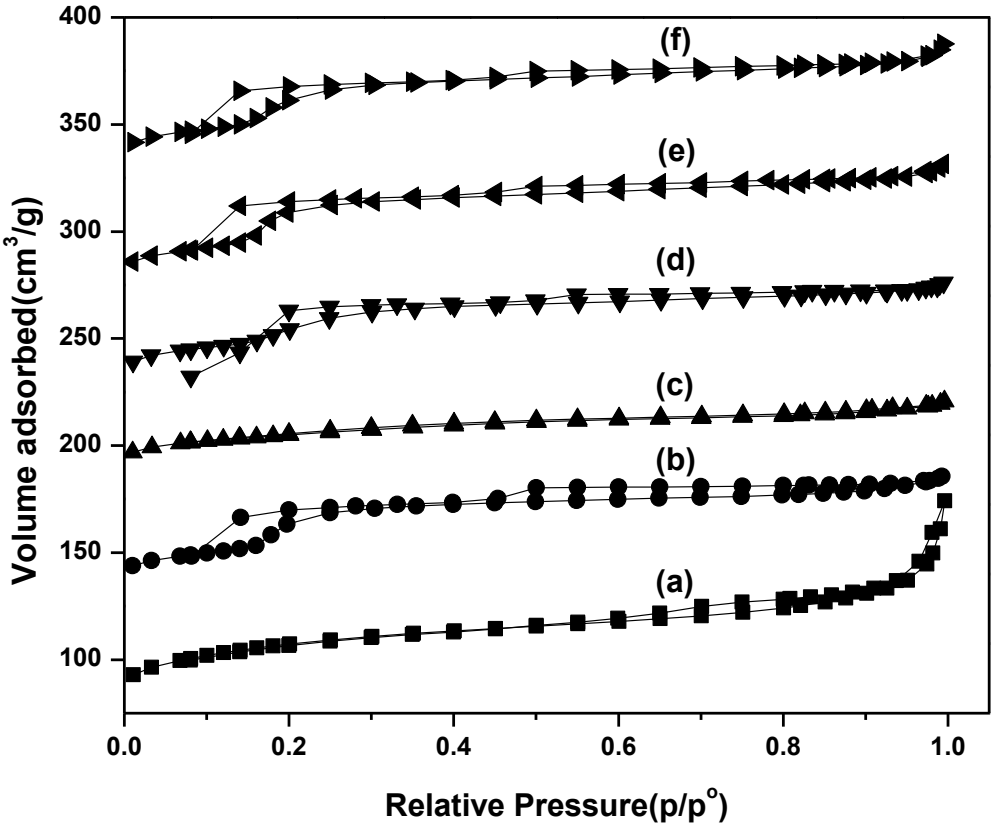

Figure 4.2 N_2 adsorption isotherm of (a) Z-30 (b) Z-280 (c) Z-1500 (d) St-Z-280 (e) DS-Z-280 (f) Mn-Z-280

Modification of the parent Z280 by steaming led to a slight decrease in the total number of acid sites from 0.3mmol NH_3/g to 0.29 mmol NH_3/g. This signifies that Z280 is of high hydrothermal stability. The acidity of St-Z-280 and Mn-Z-280 was similar to parent Z-280, whereas DS-Z-280 showed slightly higher acidity at low temperature.

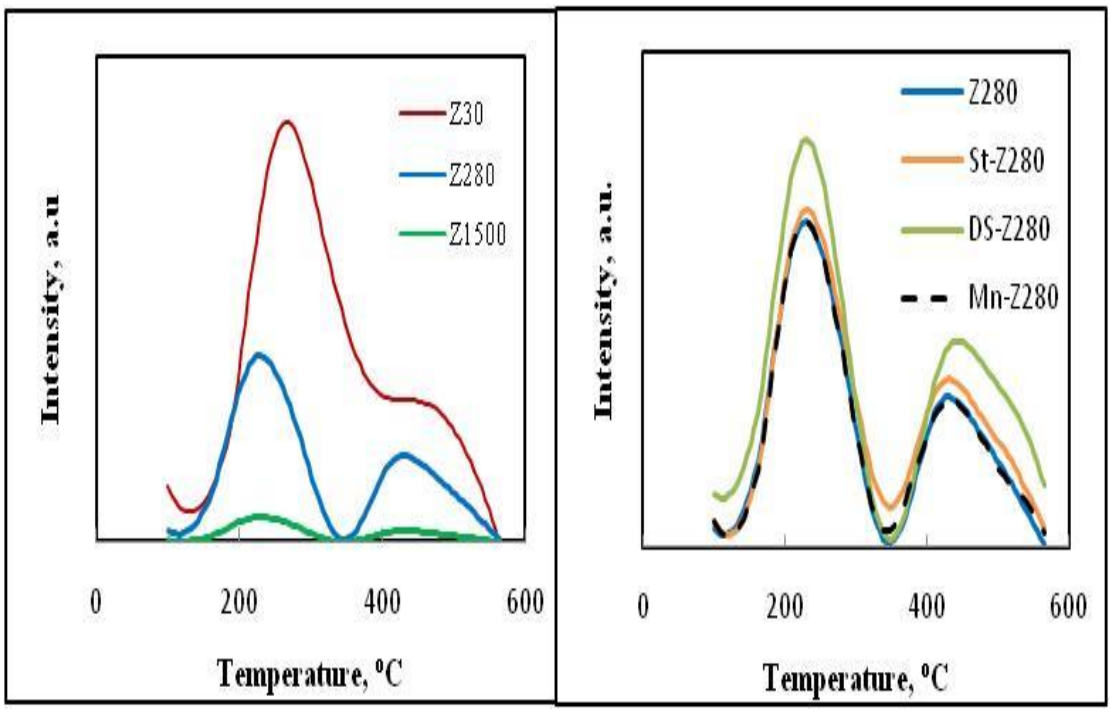

Figure 4.3 NH_3-TPD profiles of ZSM-5 additives (Z30, Z280, Z1500) and modified ZSM-5 (St-Z280, DS-Z280, Mn-Z280).

Table 4.1 Physico-chemical Properties of ZSM-5 Additives.

ZSM-5 additive	Z30	Z280	Z1500	St-Z280	DS-Z280	Mn-Z280
Si/Al ratio (treatment)	30	280	1500	(steamed)	(desilicated)	(Mn-modified)
BET surface area (m^2/g)	333	370	335	340	361	363
micropore volume (cc/g)	0.11	0.05	0.14	0.08	0.11	0.05
mesopore volume (cc/g)	0.15	0.15	0.05	0.11	0.33	0.16
NH_3TPD (mmol/g)						
total acidity	1.26	0.30	0.06	0.29	0.32	0.29
Weak/medium sites	0.80	0.16	0.05	0.15	0.18	0.15
Strong acid sites	0.46	0.14	0.01	0.14	0.14	0.14

SEM micrographs of the zeolite additives Z-30, Z-280, Z-1500 and modified Z-280 are shown in Figure 4.4. Z-30 has a crystal size of about 0.1-0.2 µm and Z-280 has 1-2 µm size, whereas Z-1500 has a crystal size of about 5-6 µm. After steaming there was no difference in crystal size as compared to parent material. The crystal size was slightly reduced for DS-Z-280. For Mn-Z-280 small particles about 50-100 nm size was observed that indicate the presence of Mn particles. (Figure 4.4f)

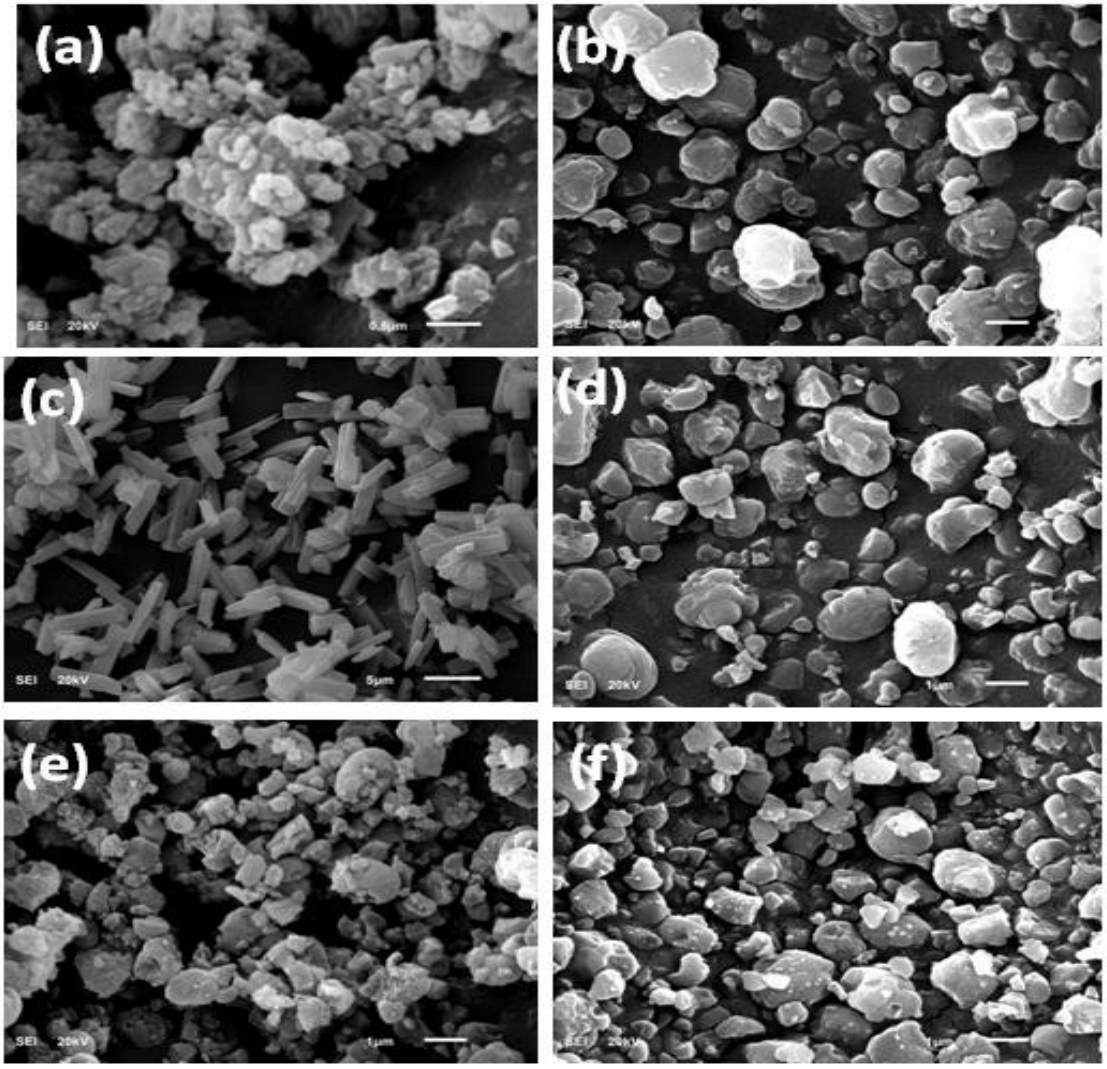

Figure 4.4 SEM images of (a) Z-30, (b) Z-280, (c) Z-1500, (d) St-Z-280, (e) DS-Z-280 and (f) Mn-Z-280

4.3 Effect of weight ratio of E-Cat and ZSM-5 additive on product yields

Arabian Light Crude oil was cracked over E-Cat/ZSM-5 mixtures that have different weight ratios. This was done to obtain the optimum percentage of additives to be added for maximum light olefins yield. Previous works [35] on the fluid catalytic cracking of vacuum gas oils have shown that maximum light olefins yield is obtained at 25 wt.% ZSM-5 additive. One additive (Z280) was tested to see its effect on light olefins yield on cracking whole crude oil.

The results obtained for the cracking of AL crude oil over E-cat/Z280 at 550°C and a catalyst/oil ratio of 3.0g/g are shown in Figure 4.5. From this figure, it can be observed that with increase in Z280 concentration from 0 to 25 wt%, there is an increase in light olefins yield from 12.1 to 20.9 wt% with a corresponding decrease in gasoline yield from 50.6 wt.% to 42.8 wt.%. Further increase in Z280 concentration from 25 to 100 wt% leads to a decrease in light olefins yield from 20.9 to 10.2 wt.% with a corresponding decrease in gasoline yield from 42.8 wt.% to 29.1 wt Hence, it can be concluded that for the fluid catalytic cracking of Arabian Light Crude Oil over a physical mixture of equilibrium catalyst and zeolite additives, 25 wt.% additives give the maximum yield of light olefins.

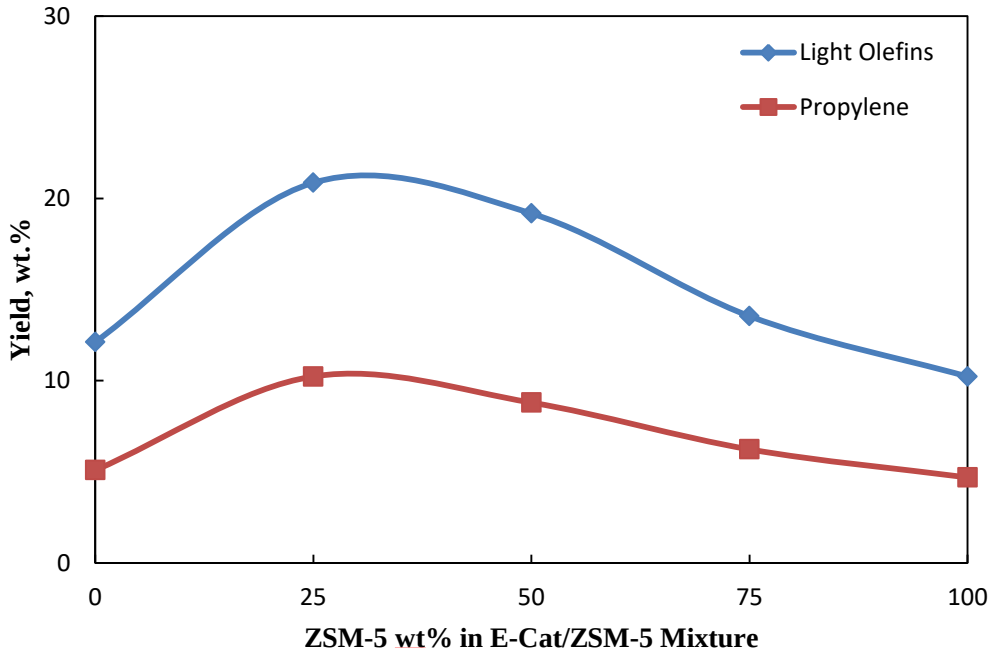

Figure 4.5 Effect of ZSM-5 on Light Olefins Yield

4.4 ASL feed

Here, the product yields obtained on cracking ASL over all the catalysts and additives used are presented with a discussion of the various yield trends.

4.4.1 Cracking of Arabian Super Light (ASL) crude oil and Vacuum Gas Oil (VGO)

The catalytic cracking of ASL over E-Cat was compared with VGO, the standard FCC feedstock. The two feeds were cracked under the same operating conditions (E-cat and 550°C) in order to compare their product yields. Figure 4.6 shows the conversion as a function of catalyst/oil ratio for ASL and VGO. For both ASL and VGO, the conversion increased with increasing C/O ratio. Between C/O ratio of 1 and 3, the conversion increased linearly, then levelled off at C/O ratio higher than 3.0. This is consistent with

the cracking of hydrocarbons in MAT units where low severity experimental conditions greatly influence the conversion [1,31].

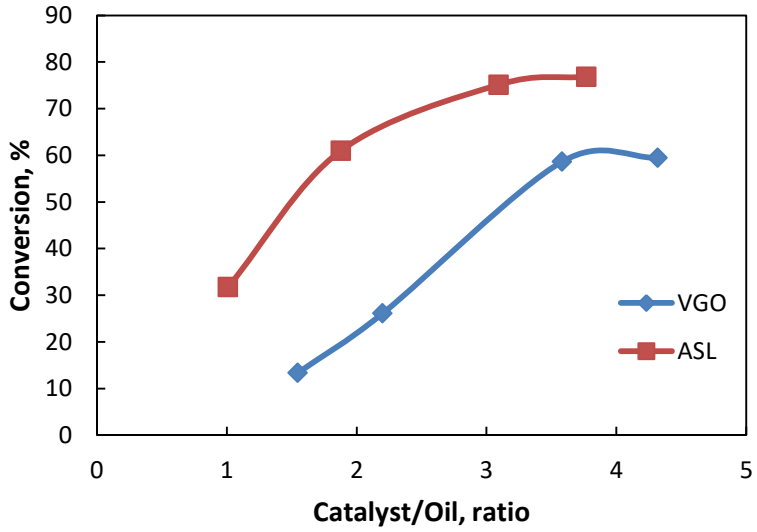

Figure 4.6 Conversion versus Catalyst/Oil for ASL and VGO cracking over E-Cat at 550°C and 60% conversion

In order to compare ASL and VGO yields favourably, product yields were calculated at a constant interpolated conversion of 60%. The products are grouped as dry gas, LPG, Gasoline, LCO, HCO and coke. Figure 4.7 shows the composition of the two feeds (ASL and VGO). It can be seen that ASL feed contains 42 wt% gasoline and 58 wt% LCO+HCO fraction while VGO feed contains 100 wt% LCO+HCO fraction. The product yields obtained on cracking both feeds over E-Cat at 550°C and 60% conversion are also shown in Figure 4.7. Here, it can be observed that ASL yields 60 wt% gasoline while VGO yields only 40 wt% gasoline. This can be explained by the fact that ASL feed already contains gasoline. Some of this gasoline in ASL remains uncracked during the

reaction [49], and also its LCO+HCO fraction further cracks to gasoline and other lighter ends which increase the overall gasoline yield.

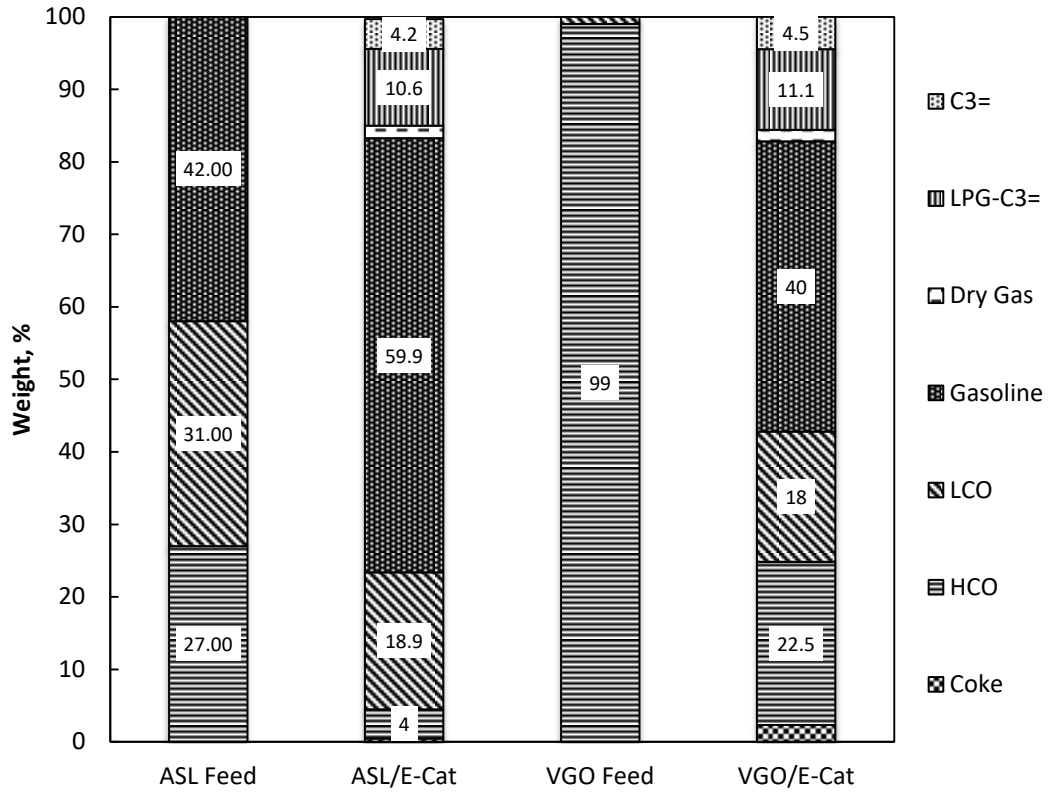

Figure 4.7 Feed composition and yield pattern of cracked products for ASL and VGO

The propylene yields obtained for both feeds are comparable as seen in Figure 4.7. This indicates that ASL can effectively replace VGO as feed in FCC units for the production of propylene and other light olefins.

Also, from Figure 4.7, it can be seen that coke yield for ASL was lower than VGO. This is because VGO has higher heavy ends fraction (100 wt%) than ASL (58 wt%). There is

also a positive linear relationship between microcarbon residue of feed (Table 3.1) and coke produced; VGO has a higher microcarbon residue than ASL.

4.4.2 Cracking Arabian Super Light (ASL) Crude Oil over E-cat and ZSM-5 additives

The Arabian Super Light (ASL) crude oil was cracked over a range of ZSM-5 additives in order to maximize the light olefins yield. The cracking was carried out at four different temperatures and four catalyst/oil ratios. The results obtained are shown in the following sections.

ASL feed was cracked over a catalyst/oil ratio range of 1-4 to obtain a wide conversion range for comparison. First, the feed was cracked over E-cat, E-cat/Z30, E-Cat/Z280 and E-cat/Z1500 as shown in Figure 4.8. The light olefins (propylene and ethylene) both increased with increasing conversion for all the catalyst additives used. The same trend was observed for the LPG, dry gas and coke yields. But for gasoline, the yield increased up to a maximum (around 70% conversion) and decreased subsequently. This suggests that above a certain conversion, some of the gasoline gets cracked to lighter ends [32]. Next, the feed was cracked over modified Z280 additive and compared with cracking over unmodified z280 (Figure 4.9). Again, the yields for all the products shown in Figure 4.8 except gasoline increased with increasing conversion.

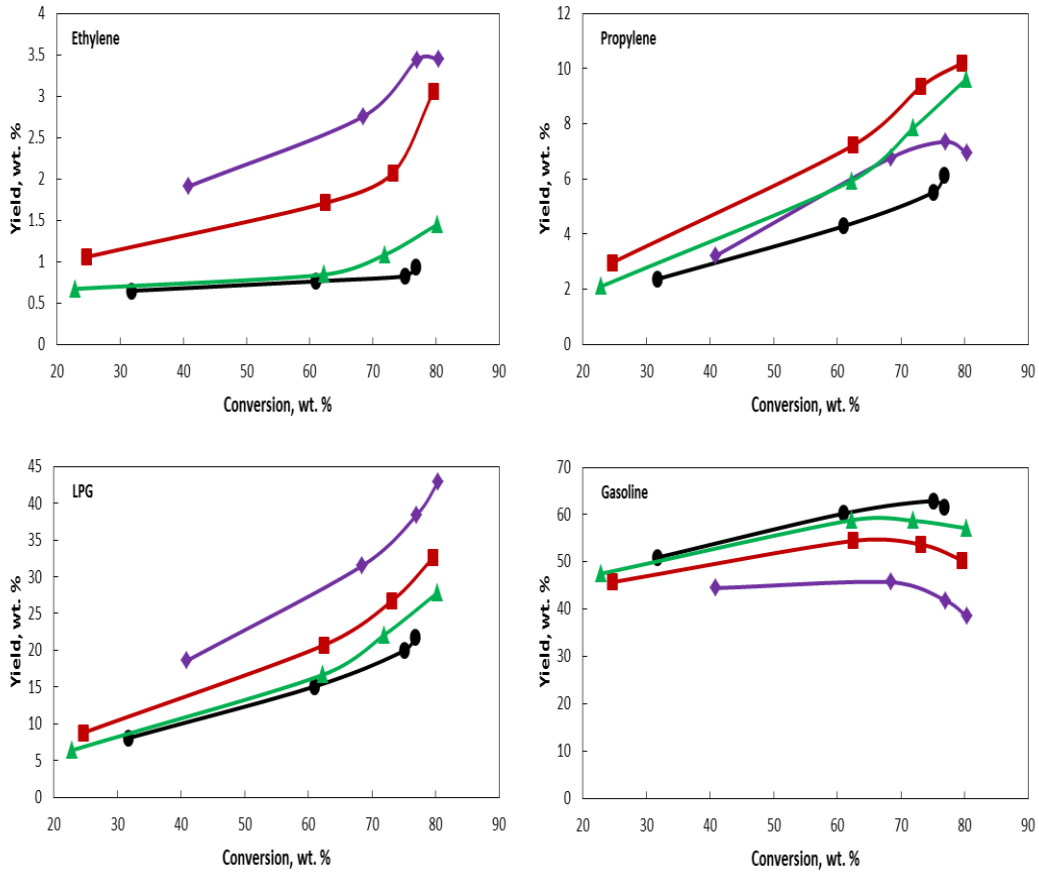

Figure 4.8 Product yields versus conversion for cracking ASL feed in MAT at 550 °C over (●) E-Cat, (♦) E-Cat/Z30, (■) E-Cat/Z280, (▲) E-Cat/Z1500

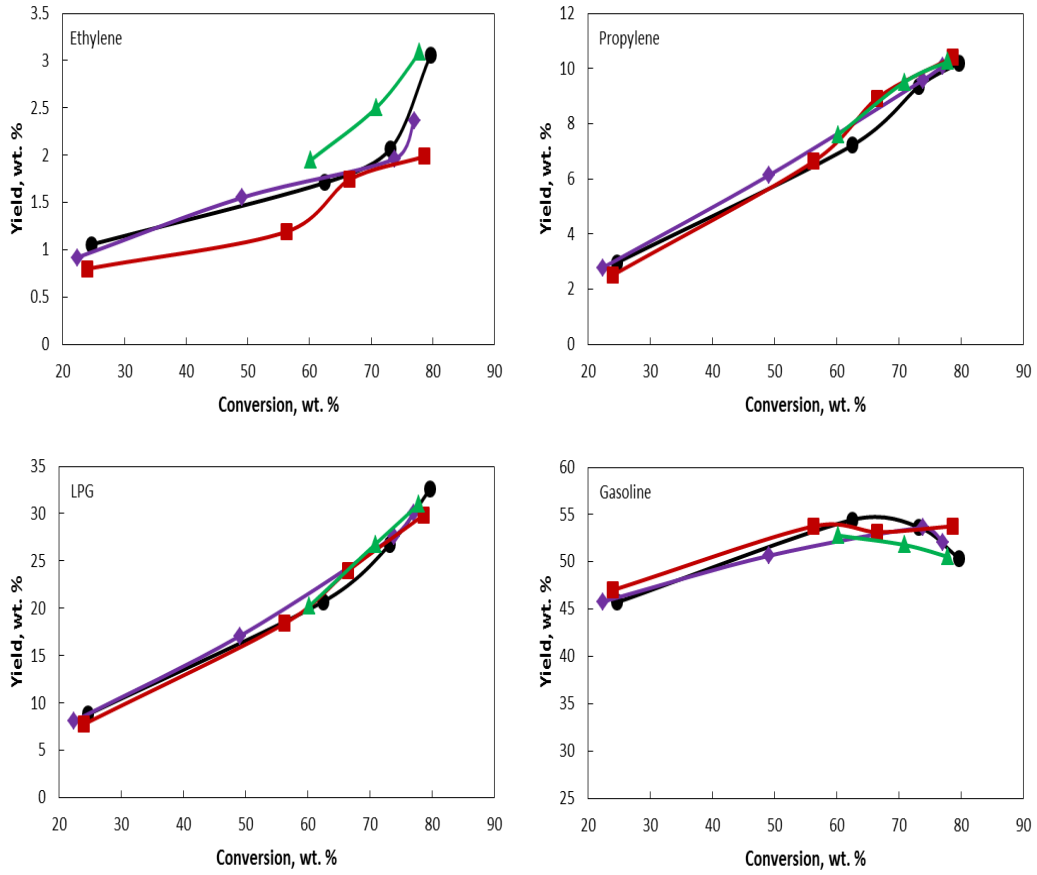

Figure 4.9 Product yields versus conversion for cracking ASL feed in MAT at 550 °C over (●) E-Cat/Z280, (♦) E-Cat/St.Z280, (■) E-Cat/MnZ280, (▲) E-Cat/DSZ280

4.4.3 Activity of ZSM-5 additives

The catalyst/oil ratio at a constant conversion gives an indication of the activity of the catalysts. Table 4.2 shows the C/O at a constant conversion of 60% for E-cat and E-cat/additives. The activity for E-cat/Z-30 blend was the highest because the lowest C/O ratio of 1.7 was required to obtain 60% conversion. The activity of the E-cat/additives decreased in the following order: Z-30>Z-280>MnZ280>Z-1500>DSZ280>St-Z-280. Activity decreases with increasing Si/Al ratio of ZSM-5. The activity is influenced by the acidic properties and the pore structure of the catalysts. High activity of Z-30 is attributed

to it strong acidity. Lowest activity for Z-1500 is due its weak acidity and low external surface area.

Table 4.2 Comparative MAT data at a constant conversion of 60% obtained by cracking of ASL crude over Ecat and Ecat/additives

ASL		Ecat/Additives					
	E-CAT	Z30	Z280	Z1500	St.Z280	Mn Z280	DSZ280
C/O ratio	1.9	1.7	1.9	2.2	2.4	2.1	2.3
Dry Gas	1.7	4.2	2.6	1.7	2.7	2.2	3.0
H_2	0.0	0.1	0.0	0.0	0.1	0.0	0.1
C_1,methane	0.5	0.6	0.4	0.4	0.5	0.4	0.5
$C_2^=$	0.8	2.5	1.7	0.8	1.7	1.3	2.0
C_2, ethane	0.4	1.0	0.5	0.4	0.5	0.4	0.5
LPG	14.8	27.5	19.9	16.1	21.7	20.2	20.2
$C_3^=$	4.2	6.4	6.9	5.7	7.7	7.3	7.6
C_3	0.7	8.2	1.9	0.7	1.8	1.3	1.9
$C_4^=$	5.0	5.0	5.9	5.6	6.3	6.2	6.1
n-C_4	2.0	3.7	2.2	1.7	2.4	2.2	2.0
i-C_4	3.0	4.3	3.0	2.3	3.6	3.2	2.7
$C_2^=$ - $C_4^=$	9.9	13.4	14.5	12.2	15.7	14.8	15.7
LPG- $C_3^=$	10.6	21.2	13.0	10.4	14.1	12.9	12.6
Gasoline	59.9	45.3	53.9	58.2	52.0	54.0	52.8
LCO	18.9	16.8	18.2	18.8	17.1	18.3	18.3
HCO	3.8	5.5	4.2	3.7	5.2	4.2	4.1
Coke	0.46	0.36	0.61	0.88	0.72	0.58	0.69
HTC	1	1.6	0.88	0.7	1.0	0.9	0.76
$C_3^=$/LPG	0.3	0.2	0.4	0.4	0.4	0.4	0.4
C_3 olefinicity	0.9	0.4	0.8	0.9	0.8	0.9	0.8
C_2 olefinicity	0.7	0.7	0.8	0.7	0.8	0.8	0.8
$\%C_3^=$/gasoline	-	3.5	10.7	20.4	10.2	12.1	11.2
CMR	0.6	1.0	0.9	0.7	0.8	0.7	1.1
GC-RON	76	85	77	77	76	71	76

4.4.4 Effect of ZSM-5 Si/Al Ratio

To compare the relative performance of the additives in the Fluid Catalytic Cracking of Arabian Super Light, product yields were compared at a constant interpolated conversion of 60%. These results are presented in Table 4.2. Two important parameters are used to explain the effect of catalysts on product yields. The first is Hydrogen Transfer Coefficient (HTC). It is defined as the ratio of butanes to butenes. It gives an indication of the tendency of the catalysts to undergo hydrogen transfer reactions [32]. Hydrogen transfer reactions consume light olefins (which are intermediate products in the catalytic cracking process) to form undesirable paraffins. Hence, for high light olefins production, low HTCs are required. HTC is a measure of hydrogen transfer activity of a catalyst with respect to feed composition. It is a bimolecular reaction that requires feed components to be in close proximity to a strong acid site [3]

The next parameter of importance is the % increase in propylene yield per unit decrease in gasoline yield (%$C_3^=$/gasoline). This is an important parameter because it shows the extent at which propylene yield is increased at the expense of gasoline yield [35].

MAT results showed that at constant conversion (60%) the C/O ratio increased with increasing Si/Al ratio. C/O increased from 1.7 for Z30 to 2.2 for Z1500. This indicates that the activity of E-Cat/ZSM-5 decreased with increasing Si/Al ratio, corresponding to the drop in the acidity of the additives [32].

At constant conversion, the yield of LPG decreased with increasing Si/Al ratio. For ASL, LPG decreased in the order Z30 (28 wt.%) > Z280 (20 wt.%) > Z1500 (16 wt.%) > E-Cat (15 wt.%). LPG is produced by the cracking of reactive species of the feed's gasoline-range hydrocarbons. Propylene yields were enhanced over E-Cat/ZSM-5, when compared

with E-Cat for ASL. Propylene yield increased with increasing Si/Al ratio and decreased on further increase of Si/Al ratio. Over Z-30, propylene yield was 6.4 wt%, it increased to 6.9 wt.% over Z-280 and then decreased to 5.7 wt% over Z-1500. As shown in Table 4.2, hydrogen transfer coefficient (HTC) decreased with increasing Si/Al ratio from 1.6 over Z-30 to 0.7 ,over Z-1500. Although HTC was lowest for Z-1500, it still gave the lowest propylene and light olefins yields. This might probably be due to the weak and low density acid sites on Z-1500 (Table 4.1), which reduces its ability to over-crack gasoline This is supported by the highest gasoline yield obtained for Z-1500 (Table 4.2 and Figure 4.10).

In Table 4.2, the maximum yield in propylene and light olefins was observed over E-Cat/Z280. For ASL feed, maximum light olefins yield was 14.5 wt. %. The presence of maxima in propylene and light olefins yields suggest the unique interplay of two balancing factors: the catalyst ability to crack gasoline-range species to light olefins and its capability to preserve light olefins from saturation to paraffins [33]. Over Z280, it appears a balance was achieved between suppression of hydrogen transfer reactions and ability to over-crack gasoline to light olefins. The hydrogen transfer coefficient (HTC) decreased with increasing Si/Al ratio for this feed.

At 60% conversion, Z-30 gave the highest ethylene yield of 2.5 wt. % and ranged between 1-2 wt.% over all other additives. Ethylene is formed through primary carbenium ion mechamism. The increase in ethylene yield over E-cat/additives compared with E-cat, may be attributed to their smaller pore structure which provides stronger interactions between catalytic surface and the carbenium ion.

The increase in dry gas yield over E-Cat/ZSM-5 compared to E-Cat is mainly due to the increase in ethylene yield which is formed via primary carbenium ion mechanism [30]. Similar to LPG yield, dry gas yield decreased with increasing Si/Al ratio for ASL.

Gasoline yield increased with increasing conversion at lower conversion and it dropped at higher conversions, as shown in Figure 4.10. Over E-cat, gasoline yield increased from 51 wt.% to 63 wt. % between conversion of 30-75% and it dropped to 61% at higher conversion of 75%. Although the yield was lower over E-cat/additives compared with E-cat, similar trend was observed over all the E-cat/additives. At 60 % conversion, gasoline yield over E-cat was 60 wt. % and it decreased to 45-53 wt.% over E-cat/additives. The gasoline yield increased with Si/Al ratio of ZSM-5 additives from 45 wt. % over Z-30 to 58 wt. % over Z-1500. This trend corresponds well with the decreasing acidity trend of Z-30, Z-280 and Z-1500 additives. This gasoline penalty or equal trade-off was mainly due to the cracking of gasoline reactive species to gaseous products (LPG) over ZSM-5 [31]. Although over Z-30 gasoline cracking was the highest (decreased from 60 wt.% over E-cat to 45 wt.%), it did not exhibit the highest olefins selectivity. This may be attributed to its highest HTC of 1.6 (Table 4.2). Results in Table 4.2 show that an inverse correlation exists between increased gasoline yield and decreased LPG yield.

Coke yields increased with increased conversion for E-cat and E-cat additives (Figure 4.8 and Figure 4.9), though the amount of coke was low (0.2 to 1 wt.%). Coke yield increased with increasing Si/Al ratio from 0.46 to 0.88 wt.% at 60% conversion for the ZSM-5 additives used.

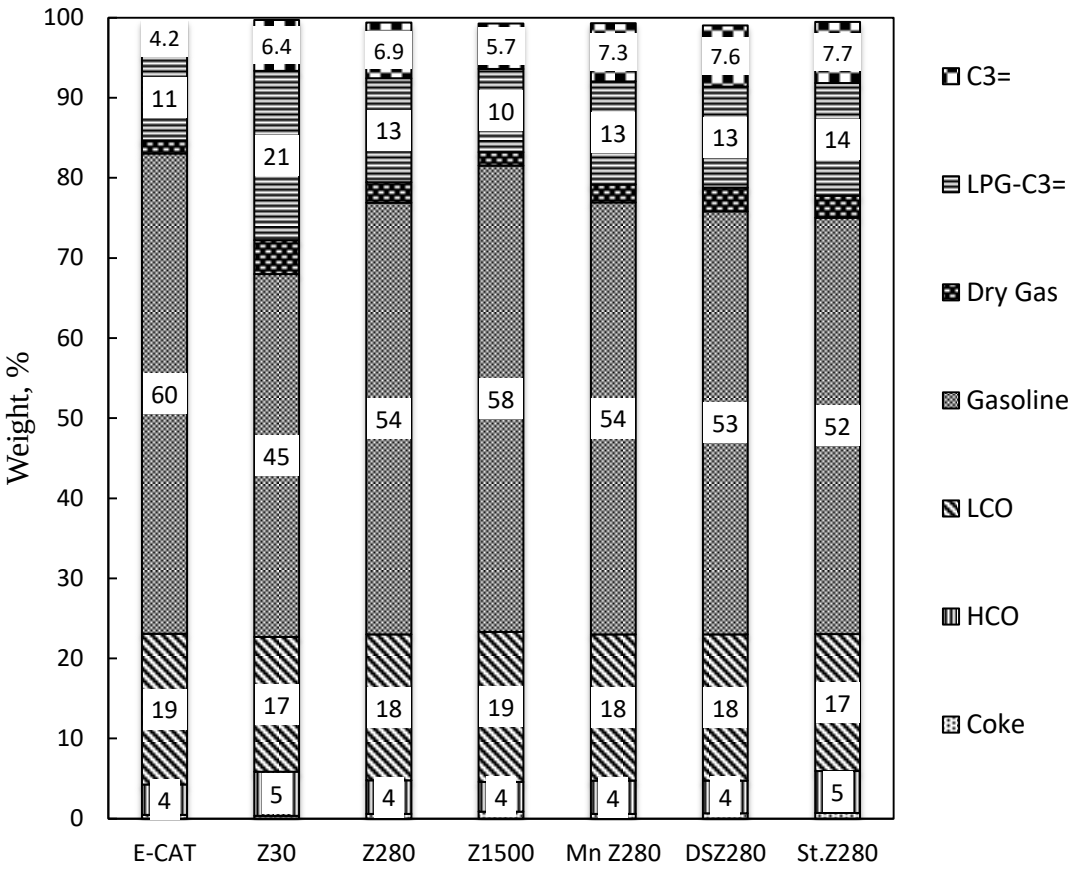

Figure 4.10 Yield patterns of cracked products for ASL over E-Cat and E-Cat/ZSM-5 at 550°C and 60 % conversion.

The composition of gasoline (paraffins, olefins, naphthenes and aromatics) in the fresh feed and cracked products over E-Cat and E-Cat/ZSM-5 at 60 % conversion is shown in Figure 4.11. Gasoline fractions in fresh ASL have paraffins content of 66 wt%, aromatics content of 15 wt.% and naphthenes of 19 wt.%.

Paraffins in the fresh ASL gasoline cut were cracked to 13.5 wt.% over E-Cat/Z30 compared with about 35.4 and 29.7 wt.% over Z280 and Z1500, respectively. Among the three additives, paraffins cracking activity was the highest over Z30 due to its highest

acidity. The decreasing cracking activity with increasing Si/Al matches well with the decreasing acidity of the ZSM-5 additives shown in Table 4.1.

The gasoline-range olefins are mainly formed by the cracking of paraffins reaching 42 wt% over E-Cat for ASL. However, upon the addition of ZSM-5 to E-Cat, the formation olefins were significantly reduced due to their conversion to aromatics and light olefins. Over Z-30, olefins content was 23 wt.% for ASL. Olefins content increased with the increase in Si/Al ratio to about 39 wt.% over Z1500 for ASL. The naphthenes content in ASL gasoline dropped from 19 to 10 wt.% over E-Cat and all the additives.

The aromatics content increased greatly for the cracked gasoline over E-Cat and the three ZSM-5 additives. For ASL, gasoline aromatics increased from 15 wt.% over E-Cat and then reached a maximum of 51 wt.% over Z30 compared with 25 and 19 wt.% over Z280 and 1500, respectively. This observation is attributed to the difference in strong acid sites within the ZSM-5 additives. The aromatization of gasoline range paraffins were significantly accelerated over Z30, which possesses strong acid sites compared with Z280 and Z1500 which have lower amount of strong acid sites [34].

As for GC-RON, the highest value of 85 was obtained over Z30 for ASL reflecting the highest content of octane enhancing aromatics. The other two additives showed lower RON values at 77 which is attributed to the bimolecular HT reaction. The higher acid sites in Z30 explain the higher HT rate leading to higher aromatics content in in Z30 and therefore higher RON.

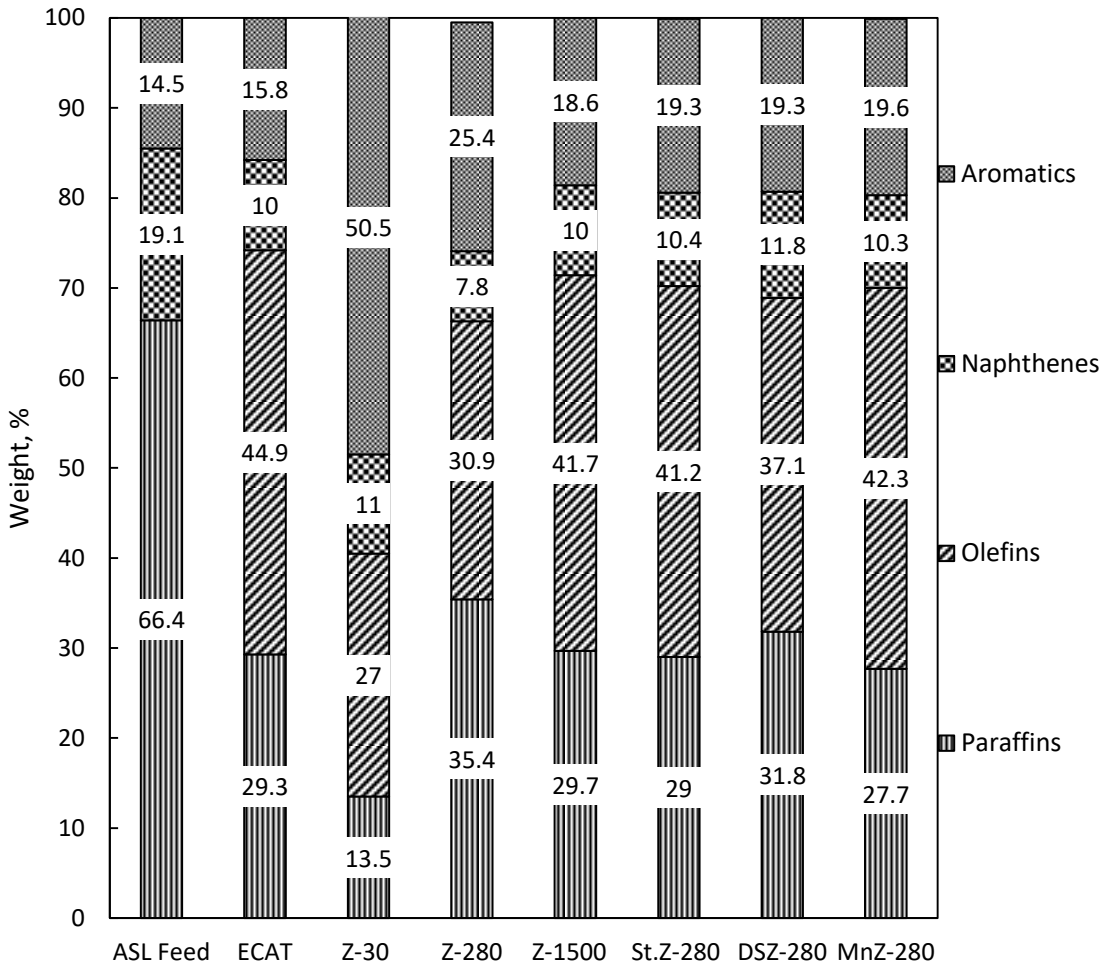

Figure 4.11 Gasoline composition of fresh and cracked ASL feed over E-Cat and E-Cat/ZSM-5 at 550°C and 60 % conversion.

4.4.5 Effect of Z280 Modification on Product Yields

Based on MAT results of cracking of ASL over various ZSM-5 additives and our previous investigation [35], Z280 was modified by Mn (2.0 wt.%), alkaline and steam treatment to further enhance the yield of propylene from the cracking of ASL. Propylene and light olefins yields were slightly enhanced (8 wt.%) over St.Z-280 and DSZ-280 compared with Z-280 (7 wt%), as shown in Table 4.2. There was insignificant effect on light olefins yields over Mn-Z280. Higher light olefins yields over St. Z-280 and DSZ-

280 was due to the mesoporosity induced by steaming and desilication. The mesopore volume was increased from 0.15 cc/g for Z-280 to 0.33 cc/g for DSZ-280 and 0.25 for St-Z-280. High mesoporosity increases the ability of catalysts to suppress the hydrogen transfer reactions, as evident from lower HTC of 0.76 for DSZ-280 compared with 0.88 HTC for Z-280 as shown in Table 4.2.

All the additives enhanced the propylene yield at 60% conversion relative to E-cat. With increase in conversion from 20 to 80%, the propylene yield also increased from approximately 3 to 10 wt% for all the E-Cat/additives. At 60% conversion, DSZ280 and St.Z280 additives gave the highest propylene yields of 7.6 wt%, closely followed by Mn280 (7.3 wt%). Modification of Z-280 by steaming, desilication and Mn-impregnation led to approximately 1wt. % increase in LPG yield. However, the composition of LPG comprising propane, propylene, normal and iso-butane and butenes, was different among the various additives

1. Effect of Mn modification

Previous work [35] has shown that Mn impregnation of ZSM-5 leads to increased light olefins yield in the catalytic cracking of VGO. As a result, the Z280 additive was impregnated with Mn to increase light olefins yield in the Fluid Catalytic Cracking of ASL.

The product yields from the cracking of ASL over E-Cat/Mn-Z280 are presented in Table 4.2. The yield patterns of the cracked products are shown in Figure 4.10. From Table 4.2, it can be seen that propylene yield increased from 6.9 wt.% for Z280 to 7.3 wt.% for Mn-Z280. This increase can be attributed to may be attributed to narrowing of Z280 pores

owing to the presence of MnO_2 clusters with low amount of Mn ions at the cation exchange sites [35]. It can also be seen that the HTC for Mn-Z280 is slightly lower than that for Z280. Gasoline, LPG and coke yields obtained over both additives were almost the same, which indicates that Mn-impregnation does not greatly affect their yields.

Although, the gasoline yields for ASL (54 wt.%) over Mn-Z280 were similar to Z280, the percent increase in propylene per unit loss in gasoline yield was higher for Mn-Z280 because of the greater propylene yield of the latter.

PIONA analysis showed a slight change in the composition and RON of cracked gasoline except for olefins and aromatics contents as shown in Figure 4.11. For ASL, olefins increased from 26 to 42 wt.% and aromatics decreased from 25 to 20 wt.% over Z280 and Mn-Z280, respectively. The change in gasoline olefins and aromatics contents may be attributed to narrowing of Z280 pores owing to the presence of MnO_2 clusters with low amount of Mn ions at the cation exchange sites [33]. The GC-RON decreased from 77 to 71 due to manganese impregnation.

2. Effect of alkaline treatment

Previous works [25,26] have shown that desilication of ZSM-5 additives by alkaline treatment leads to increased light olefins yield in the catalytic cracking of VGO. For our ASL feed, the product yields obtained on cracking over DS-Z280 are shown in Table 4.2. It can be seen that the propylene yield increased considerably from 6.9 wt.% (Z280) to 7.6 wt.% (DSZ280) while total light olefins yield increased from 14.5 wt.% (Z280) to 15.7 wt.% (DSZ280). However, gasoline yield did not show any change compared with the parent Z280. The enhancement in propylene yield upon alkaline treatment may be

ascribed to the creation of mesopores in DS-Z280 which possessed higher mesopore volume (0.33 cc/g) compared with Z280 (0.15 cc/g). Mesoporosity resulted in increasing the ability of the catalysts to suppress the hydrogen transfer reactions by rapid elution of products [16]. As for gasoline composition, DS-Z280 showed higher paraffins content at 31 wt% compared with 28 over Z280. Olefins and aromatic contents of the gasoline fraction over DS-Z280 were similar to that obtained over Mn-Z280. Values for GC-RON did show much change as a result of Z280 alkaline treatment for ASL feed catalytic cracking.

3. Effect of steam treatment

Steaming of the parent Z280 was carried out to elucidate the performance of Z280 additive in a commercial FCC unit after its deactivation. The MAT data in Table 4.2 show that the product yields of ASL feed were slightly changed by steam treatment of Z280. For ASL, propylene yield increased from 6.9 wt.% to 7.7 wt.% associated with a 2 wt.% decrease in gasoline yield (54 -52 wt.%).. The catalytic properties of Z280 and St-Z280 listed in Table 4.1 show only a drop in BET surface area in St-Z280 with no change in other properties. While dealumination by steaming leads to lowering of the number of acid sites, this disadvantage was more than offset by the creation of new types of acid sites [32]. Olefins and aromatic contents of the gasoline fraction over St-Z280 were similar to that obtained over Mn-Z280. The GC-RON remained almost constant at 76.

4.5 Arabian Extra Light (AXL)

Here, the product yields obtained on cracking AXL over all the catalysts and additives used are presented with a discussion of the various yield trends.

4.5.1 Cracking of Arabian Extra Light (AXL) crude oil and Vacuum Gas Oil (VGO)

The catalytic cracking of AXL over E-Cat was compared with that of VGO, the conventional FCC feedstock. The two feeds were cracked under the same operating conditions (E-cat and 550°C) in order to compare their product yields Typical plot of conversion versus C/O, for AXL and VGO is shown in Figure 4.12. For both AXL and VGO, the conversion increased with increasing C/O ratio.

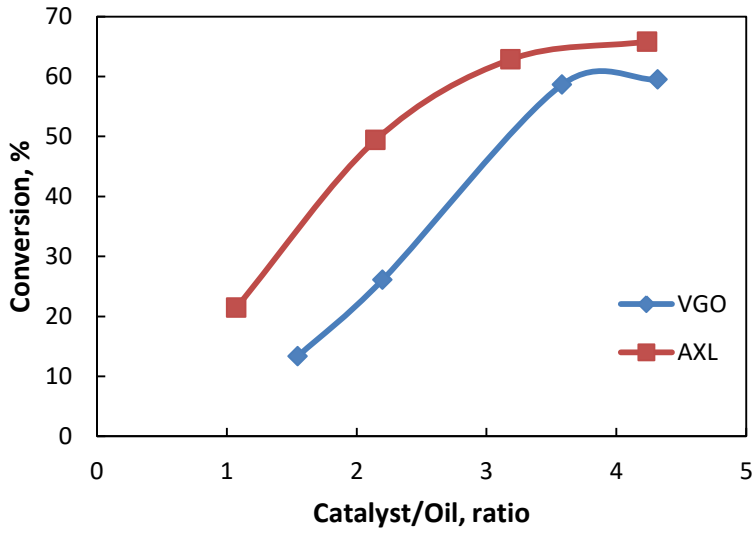

Figure 4.12 Conversion versus Catalyst/Oil for AXL and VGO cracking over E-Cat at 550°C and 60% conversion

In order to compare AXL and VGO yields favourably, product yields were calculated at a constant interpolated conversion of 60%. The products are grouped as dry gas, LPG, Gasoline, LCO, HCO and coke. Figure 4.13 shows the composition of the two feeds

(AXL and VGO). It can be seen that AXL feed contains 34 wt% gasoline and 66 wt% LCO+HCO fraction while VGO feed contains 100 wt% LCO+HCO fraction. The product yields obtained on cracking both feeds over E-Cat at 550°C and 60% conversion are also shown in Figure 4.13. Here, it can be observed that AXL yields 52 wt% gasoline while VGO yields only 40 wt% gasoline. This can be explained by the fact that AXL feed already contains gasoline. Some of this gasoline in AXL remains uncracked during the reaction [49], and also its LCO+HCO fraction further cracks to gasoline and other lighter ends which increase the overall gasoline yield.

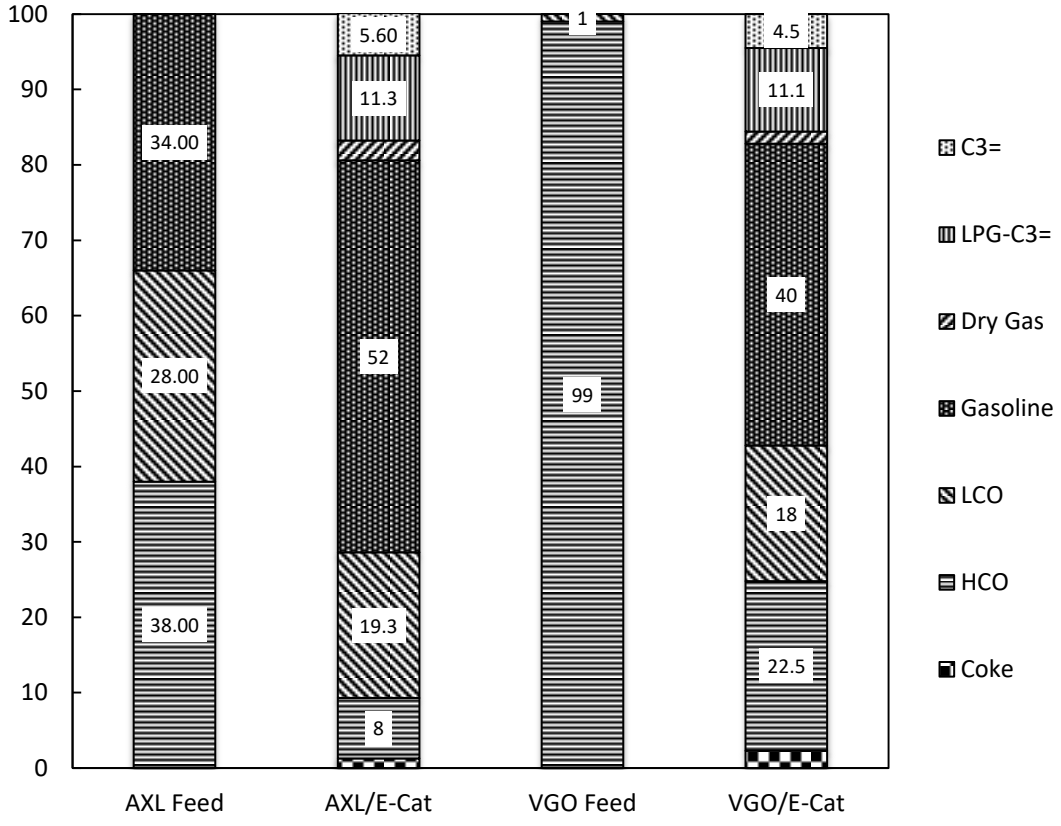

Figure 4.13 Feed composition and yield pattern of cracked products for AXL and VGO at 60 % conversion over E-Cat and 550 °C.

For both VGO and AXL, the major components obtained were LPG (15.6 and 16.9 wt% respectively) and Gasoline (40 and 52 wt% respectively) as shown in Figure 4.13. AXL produced more light olefins (13 wt%) than VGO (11.6 wt%). This indicates that AXL can also effectively replace VGO as feed in FCC units for the production of propylene and other light olefins.

4.5.2 Cracking Arabian Extra Light (AXL) Crude Oil over E-cat and ZSM-5 additives

The Arabian Extra Light (AXL) crude oil was cracked over a range of ZSM-5 additives in order to maximize the light olefins yield. The cracking was carried out at four different temperatures and four catalyst/oil ratios. The results obtained are shown in the following sections.

AXL feed was cracked over a catalyst/oil ratio range of 1-4 to obtain a wide conversion range for comparison. First, the feed was cracked over E-cat, E-cat/Z30, E-Cat/Z280 and E-cat/Z1500 as shown in Figure 4.14. The light olefins (propylene and ethylene) both increased with increasing conversion for all the catalyst additives used. The same trend was observed for the LPG, dry gas and coke yields. But for gasoline, the yield increased up to a maximum (around 60% conversion) and decreased subsequently. This suggests that above a certain conversion, some of the gasoline gets cracked to lighter ends [32]. Next, the feed was cracked over modified Z280 additive and compared with cracking over parent Z280 (Figure 4.15). Again, the yields for all the products shown in Figure 4.14 except gasoline increased with increasing conversion. It can also be observed that the gasoline yield obtained over E-cat was considerably higher than that obtained over the modified Z280 additives while the light olefins yields were much lower.

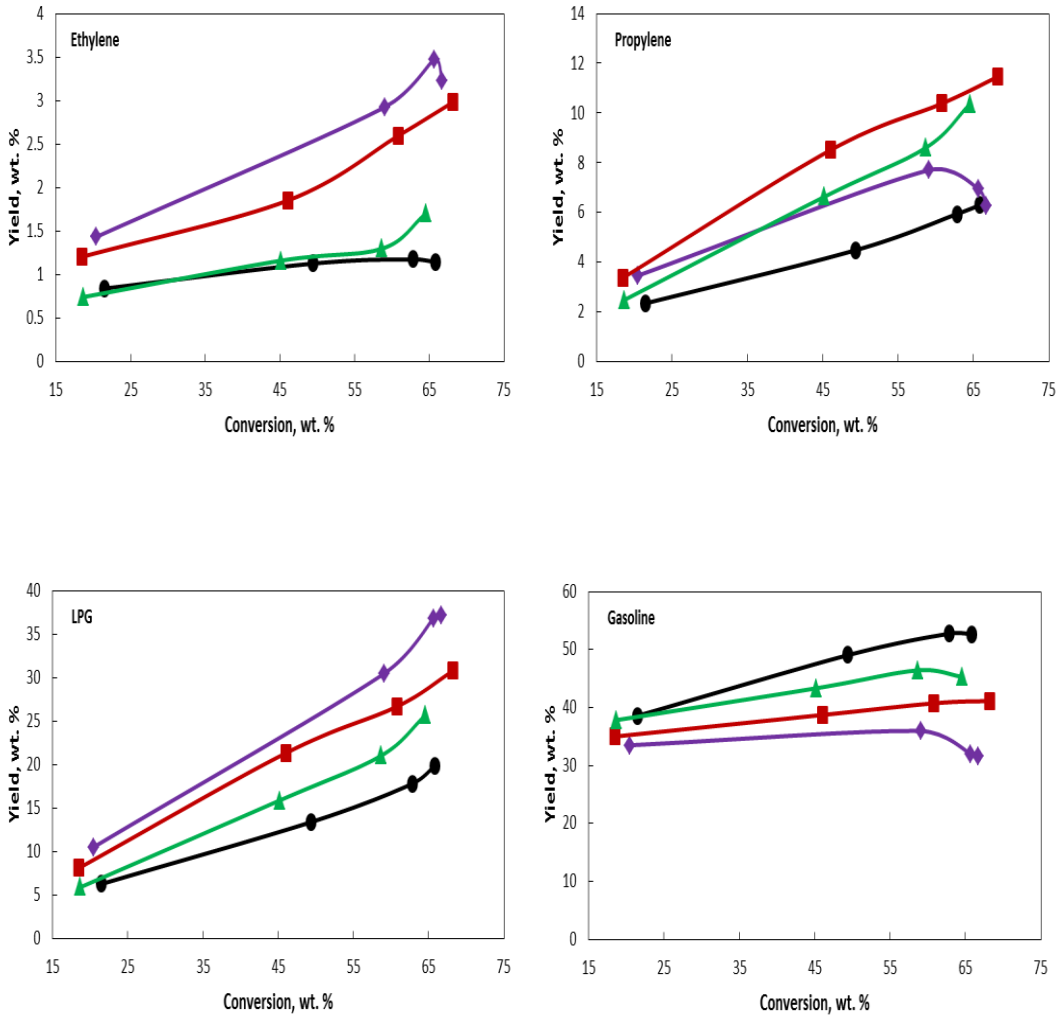

Figure 4.14 Product yields versus conversion for cracking AXL feed in MAT at 550 °C over (●) E-Cat, (♦) E-Cat/Z30, (■) E-Cat/Z280, (▲) E-Cat/Z1500

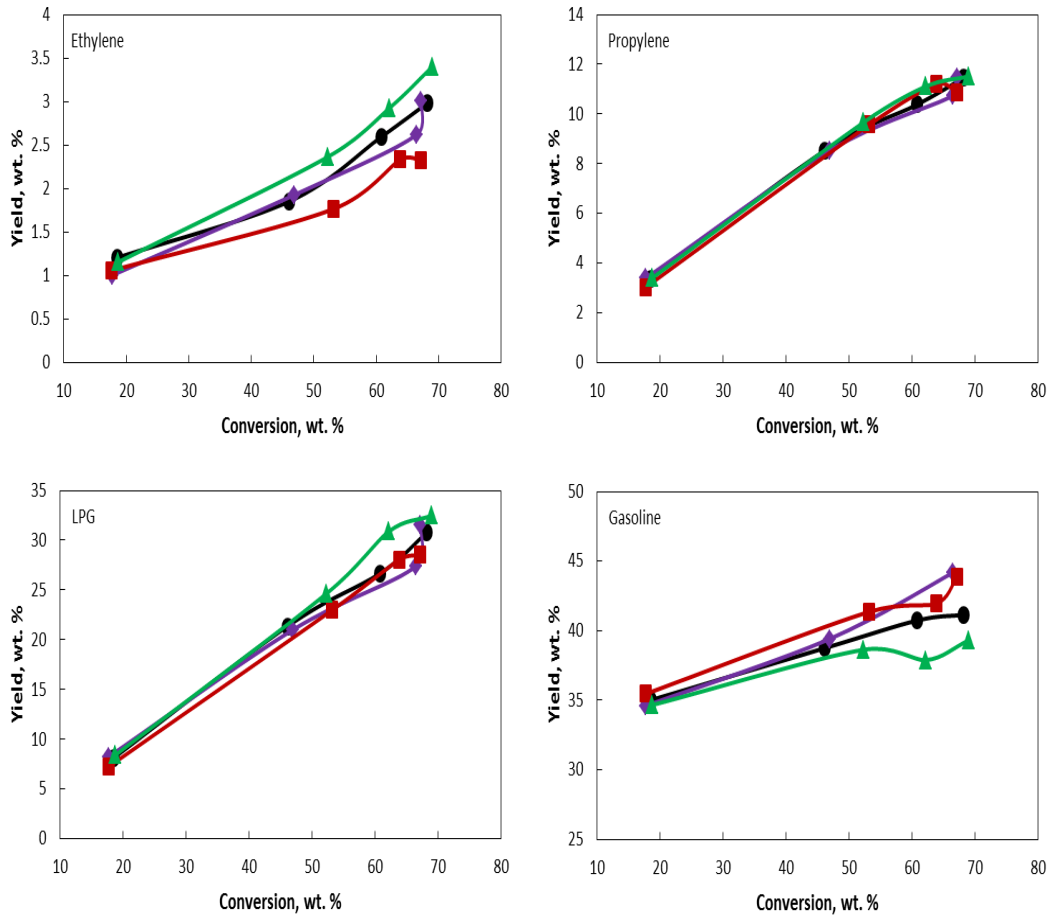

Figure 4.15 Product yields versus conversion for cracking AXL feed in MAT at 550 °C over (●) E-Cat/Z280, (♦) E-Cat/St.Z280, (■) E-Cat/MnZ280, (▲) E-Cat/DSZ280

4.5.3 Activity of ZSM-5 additives

Catalyst/Oil ratio at a constant conversion gives an indication of the activity of the catalysts. Table 4.3 shows the C/O at a constant conversion of 60% for E-cat and E-cat/additives. The activity for E-cat/Z-30 blend was the highest as the lowest C/O ratio of 2.2 was required to obtain 60% conversion. The activity of the E-cat/additives decreased in the following order: Z30>St Z280>DSZ280=MnZ280>E-Cat=Z280>Z1500. Activity decreased with increasing Si/Al ratio of ZSM-5 as was also observed with the ASL feed.

The activity is influenced by the acidic properties and the pore structure of the catalysts. High activity of Z-30 is attributed to it strong acidity (Table 4.1).

Table 4.3 Comparative MAT data at a constant conversion of 60% obtained by cracking of AXL crude over Ecat and Ecat/additives

AXL		Ecat / 25wt.% additive					
	E-Cat	Z30	Z280	Z1500	St.Z280	Mn Z280	DSZ280
C/O ratio	3.0	2.2	3.0	3.3	2.7	2.8	2.8
Dry Gas	2.6	5.3	4.3	2.8	4.0	3.6	4.3
H_2	0.1	0.1	0.1	0.1	0.1	0.1	0.1
C_1,methane	0.8	0.9	0.9	0.7	0.8	0.7	0.7
$C_2^=$	1.2	3.0	2.6	1.4	2.4	2.1	2.8
C_2, ethane	0.7	1.2	0.8	0.7	0.8	0.7	0.7
LPG	16.9	31.4	26.4	22.1	25.3	26.2	29.5
$C_3^=$	5.6	7.6	10.3	9.0	10.0	10.6	10.8
C_3	1.0	9.4	2.3	1.2	2.1	1.9	3.3
$C_4^=$	6.2	5.9	8.5	8.2	8.5	9.1	9.4
n-C_4	0.9	3.4	1.4	0.9	1.4	1.3	1.9
i-C_4	3.2	5.0	3.9	2.9	3.3	3.4	4.1
$C_2^=$ - $C_4^=$	13.0	16.5	21.3	18.5	20.9	21.8	23.0
LPG-$C_3^=$	11.2	23.8	16.1	13.1	15.3	15.6	18.7
Gasoline	52.0	35.4	40.6	46.2	42.6	41.7	38.1
LCO	19.3	16.0	16.9	18.9	16.8	17.2	16.0
HCO	6.4	10.4	9.6	7.5	9.6	9.2	10.4
Coke	1.34	1.43	1.73	2.16	1.57	1.77	1.54
HTC	0.7	1.4	0.6	0.5	0.5	0.5	0.6
$C_3^=$/LPG	0.3	0.2	0.4	0.4	0.4	0.4	0.4
C_3 olefinicity	0.9	0.5	0.8	0.9	0.8	0.9	0.8
C_2 olefinicity	0.6	0.7	0.8	0.7	0.8	0.8	0.8
%$C_3^=$/gasoline	-	2.1	7.3	10.3	8.3	8.6	6.6
CMR	0.8	1.1	1.1	1.0	1.2	1.1	1.0
GC-RON	81	88	78	78	74	77	77

4.5.4 Effect of ZSM-5 Si/Al Ratio

The product yields from the cracking of AXL over E-Cat/ZSM-5 are presented in Table 4.3. The plots of product yields versus conversion and the yield structure of cracked products are shown in Figures 4.14 and 4.15, respectively.

At 60% conversion level, LPG yield increased from 17 wt. % over E-cat to 22-31 wt. % over E-cat/additive blends (Table 4.3). The highest increase was observed for E-cat/Z-30 (31 wt.%) and the lowest increase was obtained for E-cat/Z-1500 (22 wt. %). Decreasing trend of LPG yield with increased Si/Al ratio of ZSM-5 was observed. LPG is produced by the cracking of reactive species of the feed gasoline-range hydrocarbons. Propylene yields were enhanced over E-Cat/ZSM-5, when compared with E-Cat; the extent of propylene enhancement was 84 % for AXL over E-Cat/Z280.

Propylene yield increased with increasing Si/Al ratio and decreased on further increase of Si/Al ratio. Similar trend was observed for light olefins ($C_2^=$ to $C_4^=$), as shown in Figure 4.16. On increasing the Si/Al ratio from 30 to 1500, the propylene yield increased from 7.6 wt% (Z30) to 10.3 wt% (Z280) and then dropped to 9 wt % (Z1500). The maximum yield in propylene and light olefins was observed over E-Cat/Z280. The maximum light olefins yield was 21.3 wt.% for AXL over E-Cat/Z280. The presence of maxima in propylene and light olefins yields suggest the unique interplay of two balancing factors: the catalyst ability to crack gasoline-range species to light olefins and its capability to preserve light olefins from saturation to paraffins [32]. Over Z280, a balance was achieved between suppression of hydrogen transfer reactions and ability to over-crack gasoline to light olefins. The hydrogen transfer coefficient (HTC) decreased with increasing Si/Al ratio; it decreased from 1.4 over Z30 to 0.5 over Z1500. Although HTC

was the lowest for Z1500, it yielded the lowest propylene and light olefins yields which is attributed to the weak and low density acid sites on Z1500 (Table 4.1). This is supported by the high gasoline yield obtained over Z1500 for AXL feed which is similar to E-Cat.

Propylene selectivity within LPG ($C_3^=$/LPG) decreased in the following order Z1500> >Z280>Z30 with respect to Si/Al molar ratio. This trend may be explained by the fact that high HTC decreases propylene selectivity within LPG due to conversion of propylene to propane.

The increase in dry gas yield over E-Cat/ZSM-5 compared to E-Cat is mainly due to the increase in ethylene yield which is formed via primary carbenium ion mechanism [30]. Similar to LPG yield, dry gas yield decreased with increasing Si/Al ratio.

At 60% conversion, Z-30 gave the highest ethylene yield of 3 wt. % and ranged between 1.5-2.8 wt.% over all other additives. Ethylene is formed through primary carbenium ion mechamism. The increase in ethylene yield over E-cat/additives compared with E-cat, may be attributed to their smaller pore structure which provides stronger interactions between catalytic surface and the carbenium ion.

Coke yields increased with increased conversion for E-cat and E-cat additives. At 60% conversion, while E-cat gave a coke yield of 1.34 wt %, E-cat/Z-1500 gave the highest coke yield of 2.2 wt. %.

Over E-cat, gasoline yield increased from 38.6 wt.% to 52.8 wt. % between conversion of 21-63% and it dropped slightly to 52.6% at higher conversion of 66%. Decrease in gasoline yield over modified Z-280 additives, St. Z-280, DSZZ-280 and Mn-Z-280 compared with E-cat was similar to Z-280. This might be due to their similar acidity.

Results in Table 4.3 show that an inverse correlation exists between increased gasoline yield and decreased LPG yield.

The gasoline yield increased with Si/Al ratio of ZSM-5 additives from 35 wt. % over Z-30 to 46 wt. % over Z-1500. This trend corresponds well with the decreasing acidity trend (Table 4.1) of Z-30, Z-280 and Z-1500 additives. Although over Z-30 gasoline cracking was the highest (decreased from 52 wt.% over E-cat to 35 wt.%), it did not exhibit the highest olefins selectivity. This may be attributed to its highest HTC of 1.42 (Table 4.3). This gasoline penalty or equal trade-off was mainly due to the cracking of gasoline reactive species to gaseous products (LPG) over ZSM-5 [31].

The percentage increase in propylene yield per unit decrease in gasoline yield ($\%C_3^=$/gasoline) is a good indication of the propylene selectivity from conversion of gasoline range olefins to light olefins (C_2-C_4) and a useful parameter for FCC economic evaluation. Over Z-30, Z-280 and Z-1500 ($\%C_3^=$/gasoline) increased from 2.1 to 10.3. This increase in ($\%C_3^=$/gasoline) with increasing Si/Al might be due to decrease in the decreasing HTC trend, favouring desorption of propylene from catalyst channels without being saturated to propane as evidence by the decreasing trend of propane (Table 4.3). The isomerisation and cracking reactions were accelerated by the addition of ZSM-5 for the crude oil cracking. It was shown that the ratio of cracking to isomerisation reactions is lower at higher Si/Al ratio, which results in higher gasoline yield [22]. On the other hand, coke yield increased with increasing Si/Al ratio from 1.4 to 1.9 wt.% for AXL over the three additives. The yields of LCO and HCO over Z-280 and Z1500 were similar to those obtained over E-Cat. Z30 showed higher HCO yield at 10.4 wt.% for AXL compared with 8.0 over E-Cat.

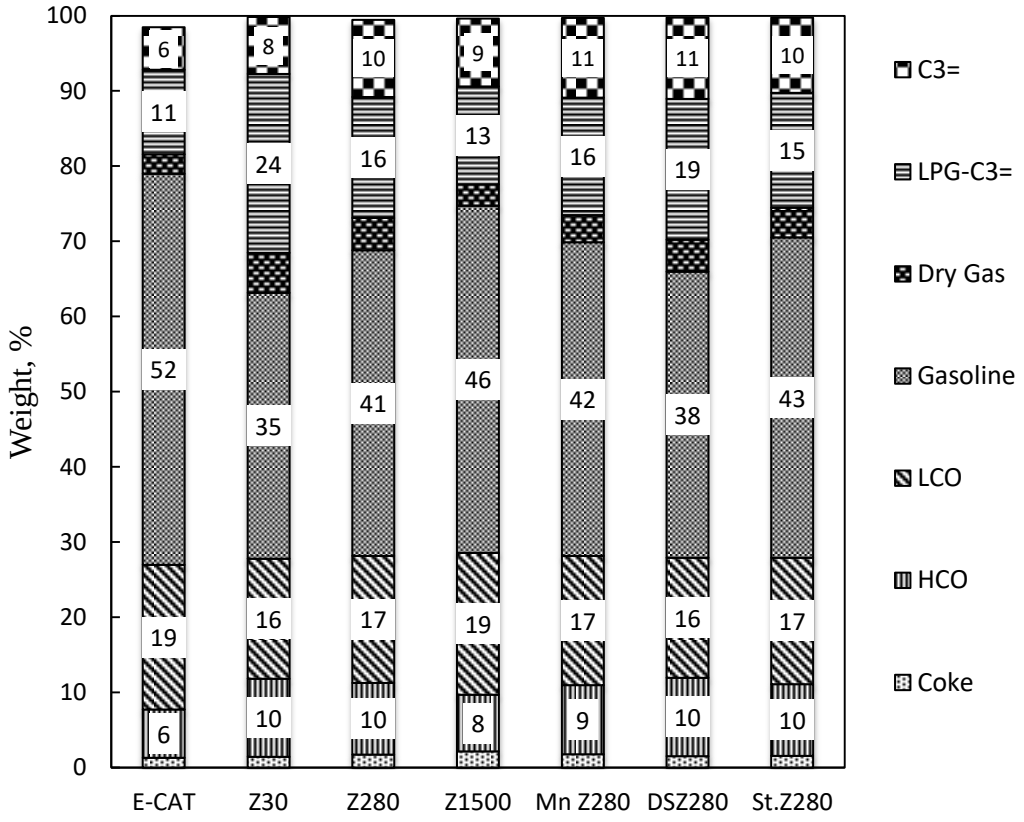

Figure 4.16 Yield patterns of cracked products for AXL over E-Cat and E-Cat/ZSM-5 at 550°C and 60 % conversion.

The composition of gasoline (paraffins, olefins, naphthenes and aromatics) in the fresh feeds and cracked products over E-Cat and E-Cat/ZSM-5 at 60 % conversion is shown in Figure 4.17. Gasoline fractions in fresh AXL feed has paraffins content of 66 wt.% , aromatics content of 27 wt.% and naphthenes of 9 wt.%.

Paraffins in the fresh AXL gasoline cut were cracked to 9.5 wt.% over E-Cat/Z30 compared with about 22 and 26 wt.% over Z280 and Z1500, respectively. The gasoline-range olefins are mainly formed by the cracking of paraffins reaching 34 wt.% over E-

Cat for AXL. However, upon the addition of ZSM-5 to E-Cat, the formation olefins were significantly reduced due to their conversion to aromatics and light olefins. The lowest content of gasoline olefins was over E-Cat/Z30, which can be attributed to its highest acidity [22].

The aromatics content increased considerably in all cracked gasolines over E-Cat and the three ZSM-5 additives. In the cracking of AXL, with gasoline aromatics content increased from 27 to 71 wt.% over Z30 compared with 43 and 34 wt.% over Z280 and Z1500, respectively. This observation is attributed to the difference in strong acid sites within the ZSM-5 additives. The aromatization of gasoline range paraffins were significantly accelerated over Z30, which possesses strong acid sites compared with Z280 and Z1500 which have lower amount of strong acid sites [36].

As for GC-RON, the highest value of 88 was obtained over Z30 for AXL, reflecting the highest content of octane enhancing aromatics. The other two additives showed lower RON value of around 77 which is attributed to the bimolecular hydrogen transfer (HT) reaction. The higher acid sites in Z30 explain the higher HT rate leading to higher aromatics content in in Z30 and therefore higher RON.

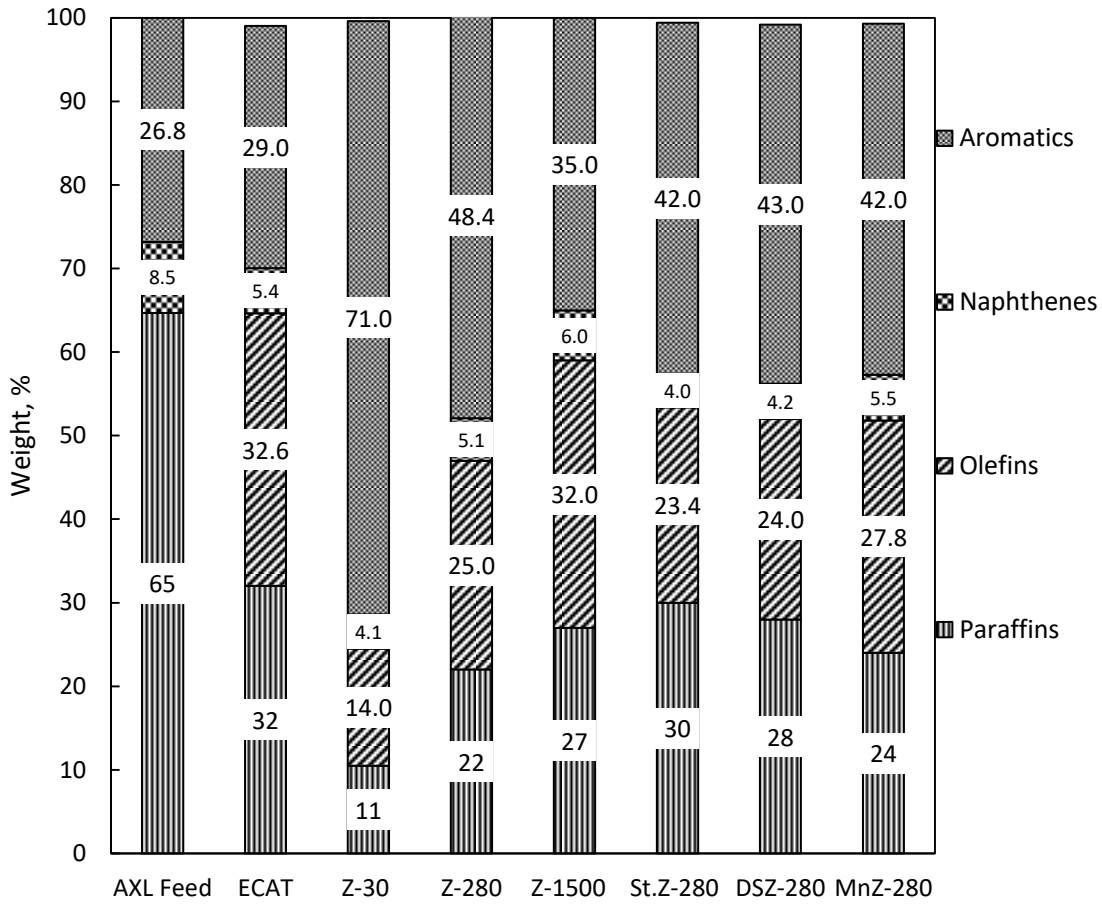

Figure 4.17 Gasoline composition of fresh and cracked AXL feed over E-Cat and E-Cat/ZSM-5 at 550 °C and 60 % conversion.

4.5.5 Effect of Z280 Modification on Product Yields

Based on MAT results and our previous investigation [35], Z280 was modified by Mn (2.0 wt.%), alkaline and steam treatment to further enhance the yield of propylene from the cracking of AXL.

Light olefins yields were slightly enhanced (21.8-23 wt%) over Mn.Z-280 and DSZ-280 compared with Z-280 (21.3 wt%), as shown in Table 4.3 and Figure 4.16. There was slight decrease in light olefins yields over St-Z280 (20.9 wt%). A higher light olefins

yield over DSZ-280 was due to the mesoporosity induced by desilication. The mesopore volume was increased from 0.15 cc/g for Z-280 to 0.33 cc/g for DSZ-280.

All the additives enhanced the propylene yield at 60% conversion relative to E-cat. With increase in conversion from 20 to 68%, the propylene yield also increased from approximately 3 to 11.5 wt% for all the E-Cat/additives. At 60% conversion, DSZ280 and Mn.Z280 additives gave the highest propylene yields of 10.8 wt% and 10.6 wt% respectively, closely followed by Z-280 (10.3 wt%). Over modified Z-280, the value of $\%C_3^=$/gasoline (6.6-8.6) was similar to Z-280 (~7.3) because of similar HTC.

1. Effect of Mn modification

The product yields from the cracking of AXL over E-Cat/Mn-Z280 are presented in Table 4.3. The yield patterns of the cracked products are shown in Figure 4.16. The results show that at 60 % conversion, the C/O over Mn-Z280 was 2.8 for AXL compared with 3.0 over Z280. For AXL, Mn-Z280 showed an enhancement in propylene yield reaching 11 wt.% associated with a decrease in propane yield compared with the parent Z280. Mn-Z280 catalyst showed slight change in the dry gas yield due to the drop in the ethylene yield. Although, the gasoline yields for AXL (42 wt.%) over Mn-Z280 were similar to Z280 (41), the percent increase in propylene per unit loss in gasoline yield was higher for Mn-Z280.

PIONA analysis showed a slight change in the composition and RON of cracked gasoline except for olefins and aromatics contents as shown in Figure 4.17. For AXL, olefins increased from 5.3 to 28.5 wt.% and aromatics decreased from 48.4 to 37 wt.% over Z280 and Mn-Z280, respectively. The change in gasoline olefins and aromatics contents

may be attributed to narrowing of Z280 pores owing to the presence of MnO_2 clusters with low amount of Mn ions at the cation exchange sites [35].

2. Effect of alkaline treatment

The product yields from the cracking of AXL feed over E-Cat/DSZ280 are shown in Table 4.3 and Figure 4.16. The effect of alkaline treatment showed an increase of 10 % in propylene yield for AXL. However, gasoline yield did show any change compared with the parent Z280. The enhancement in propylene yield upon alkaline treatment may be ascribed to the creation of mesopores in DS-Z280 which possessed higher mesopore volume (0.33 cc/g) compared with Z280 (0.15 cc/g). Mesoporosity resulted in increasing the ability of the catalysts to suppress the hydrogen transfer reactions by rapid elution of products [16]. As for gasoline composition, DS-Z280 showed higher paraffins content at 26 wt.% compared with 23 wt.% over Z280. Values for GC-RON did show any change as a result of Z280 alkaline treatment for AXL feed.

3. Effect of steam treatment

The MAT data in Table 4.3 show that the product yields of AXL were slightly changed by steam treatment of Z280. For AXL, there was no change in propylene yield and there was slight decrease in gasoline yield. The catalytic properties of Z280 and St-Z280 listed in Table 4.1 show only a drop in BET surface area in St-Z280 with no change in other properties. While dealumination by steaming leads to lowering of the number of acid sites, this disadvantage was more than offset by the creation of new types of acid sites [32]. Olefins and aromatic contents of the gasoline fraction over St-Z280 were similar to that of Z280. Gasoline paraffins in AXL increased from 23 to 30 wt.% associated with a decrease in olefins from 27 to 22 wt.% over Z280 and St-Z280, respectively.

4.6 Arabian Light Crude Oil

Here, the product yields obtained on cracking AL over all the catalysts and additives used are presented with a discussion of the various yield trends.

4.6.1 Cracking of Arabian Light (AL) crude oil and Vacuum Gas Oil (VGO)

The catalytic cracking of AL over E-Cat was also compared with VGO, the standard FCC feedstock. Typical plots of conversion versus C/O, for AL and VGO are shown in Figure 4.18. For both AL and VGO, the conversion increased with increasing C/O ratio. Between C/O ratio of 1 and 3, the conversion increased linearly for AL, then levelled off at C/O ratio higher 3.0. This is consistent with the cracking of hydrocarbons in MAT units where low severity experimental conditions greatly influence the conversion [1,31].

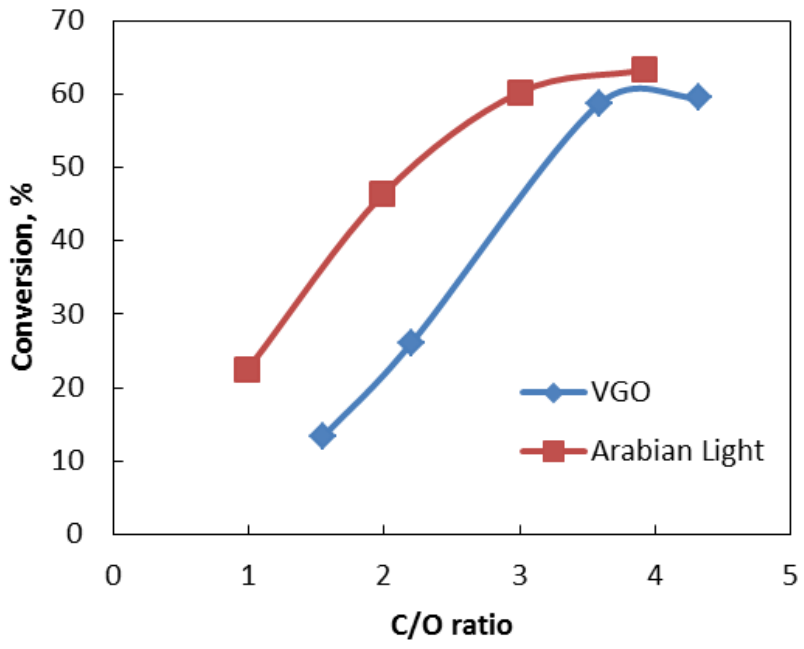

Figure 4.18 Conversion versus catalyst/oil ratio (C/O) for cracking AL and VGO over E-Cat at 550 °C

In order to compare AL and VGO yields favourably, product yields were calculated at a constant interpolated conversion of 60%. The products are grouped as dry gas, LPG, Gasoline, LCO, HCO and coke. The C/O ratios at constant conversion give an indication of the relative ease in cracking the feeds. AL requires a C/O ratio of 3.0 for 60% conversion compared to VGO which has a C/O of 4.3. This can be explained by the fact that AL has a lower 221°C^+ cut (69.2 wt%) compared to 100 wt% for VGO, meaning it contains much less hydrocarbons to be cracked.

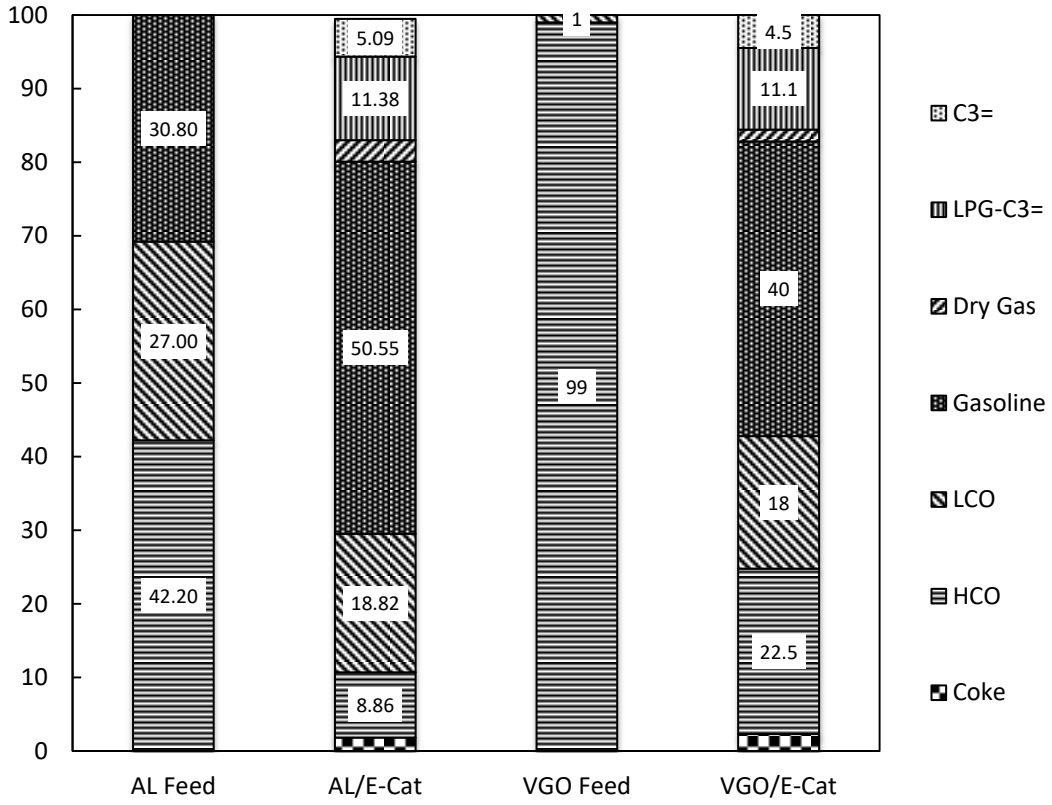

Figure 4.19 Feed composition and yield pattern of cracked products for AL and VGO at 60 % conversion over E-Cat and 550 °C.

For both VGO and AL, the major components obtained were LPG (15.6 and 16.4 wt% respectively) and Gasoline (40 and 50.6wt% respectively) as shown in Figure 4.19. AL produced more light olefins (12.1 wt%) than VGO (11.6 wt%). This may be as a result of their hydrogen transfer coefficients; 0.53 for VGO and 0.74 for AL.

4.6.2 Cracking Arabian Light (AL) Crude Oil over E-cat and ZSM-5 additives

The Arabian Light (AL) crude oil was cracked over a range of ZSM-5 additives in order to maximize the light olefins yield. The cracking was carried out at four different temperatures and four catalyst/oil ratios. The results obtained are shown in the following sections.

AL feed was cracked over a catalyst/oil ratio range of 1-4 to obtain a wide conversion range for comparison. First, the feed was cracked over E-cat, E-cat/Z30, E-Cat/Z280 and E-cat/Z1500 as shown in Figure 4.20. The light olefins (propylene and ethylene) both increased with increasing conversion for all the catalyst additives used. The same trend was observed for the LPG, dry gas and coke yields. But for gasoline, the yield increased up to a maximum (around 60% conversion) and decreased subsequently. This suggests that above a certain conversion, some of the gasoline gets cracked to lighter ends [32]. Next, the feed was cracked over modified Z280 additive and compared with cracking over E-cat/Z280 (Figure 4.21). Again, the yields for all the products shown in Figure 4.21 except gasoline increased with increasing conversion.

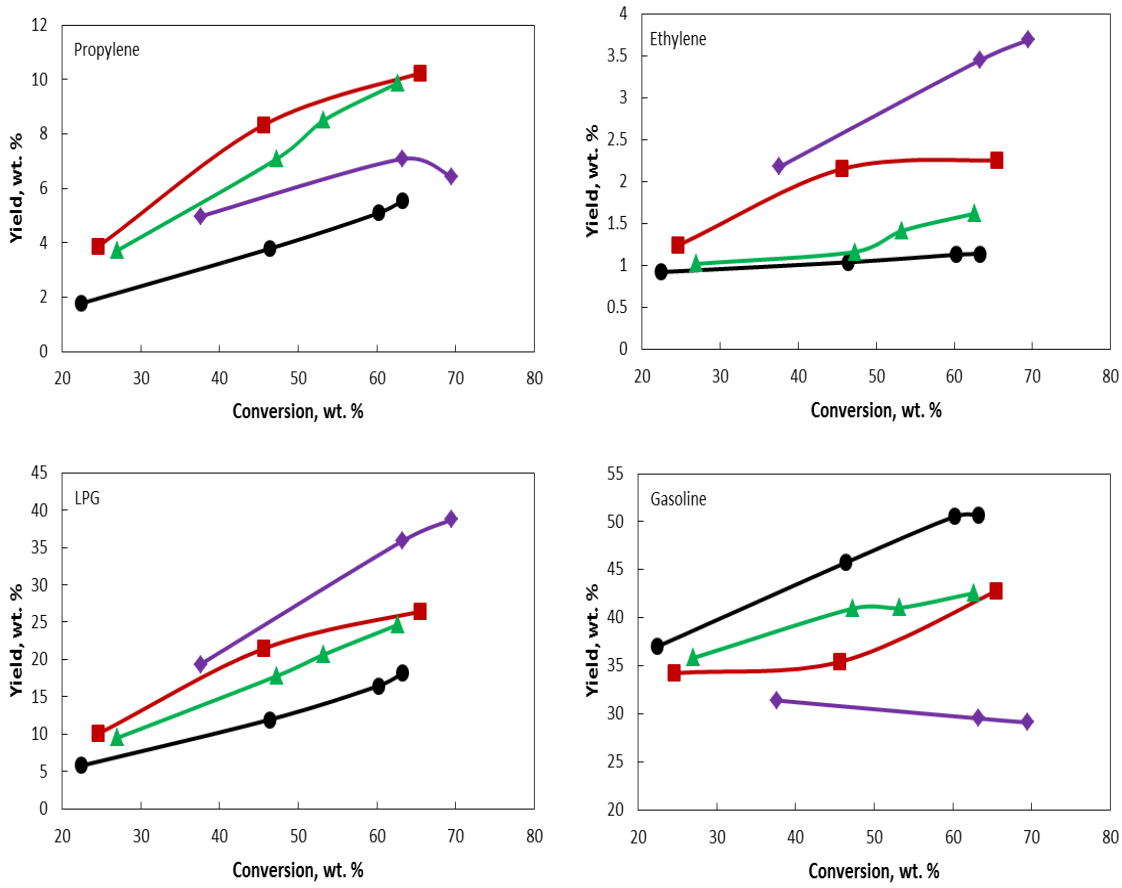

Figure 4.20 Product yields versus conversion for cracking AL feed in MAT at 550 °C over (●) E-Cat, (♦) E-Cat/Z30, (■) E-Cat/Z280; (▲) E-Cat/Z1500.

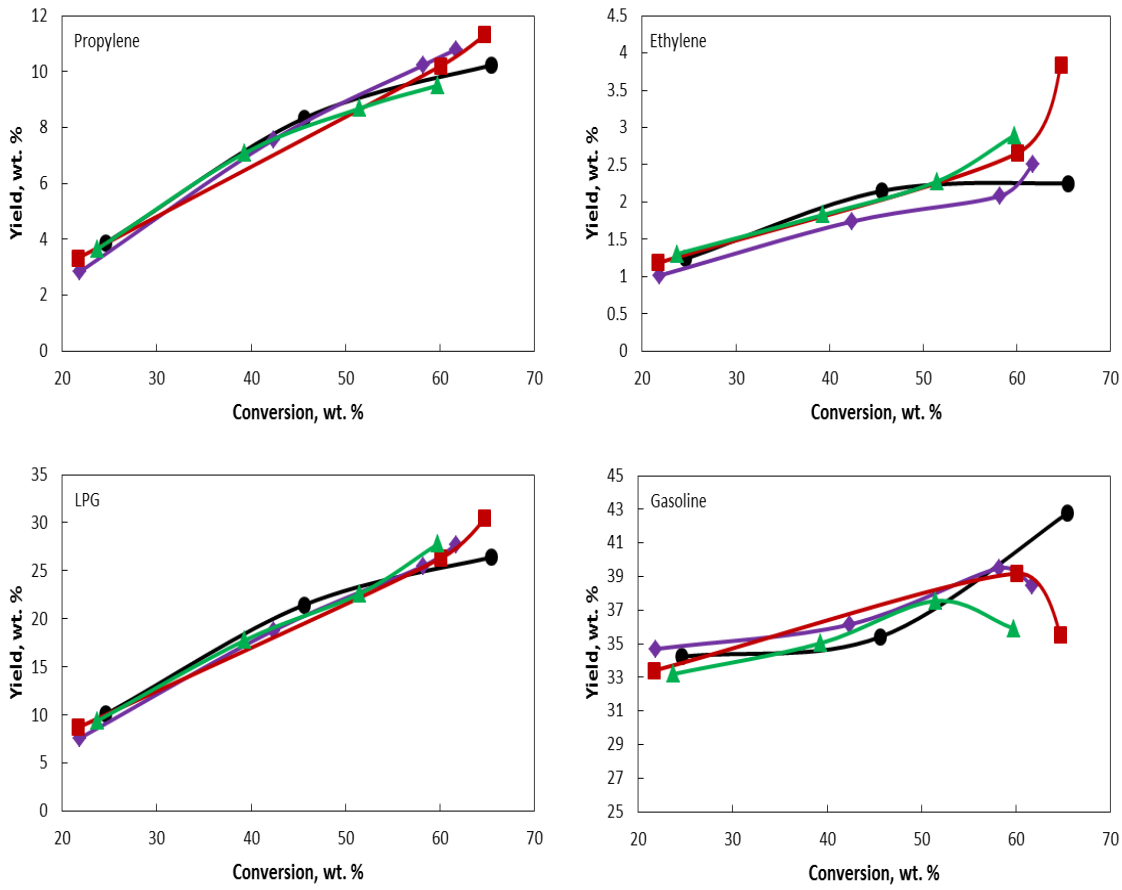

Figure 4.21 Product yields versus conversion for cracking AL feed in MAT at 550 °C over (●) E-Cat/Z-280, (♦) E-Cat/Mn-Z280, (■) E-Cat/DS-Z280; (▲) E-Cat/St.Z280.

4.6.3 Activity of ZSM-5 additives

The catalyst/oil ratio at a constant conversion gives an indication of the activity of the catalysts. Table 4.4 shows the C/O at a constant conversion of 60% for E-cat and E-cat/additives. The activities for E-cat/Z-30 and E-cat/Z280 blend were the highest because the lowest C/O ratio of around 2.9 was required to obtain 60% conversion. The activity of the E-cat/additives decreased in the following order: Z-30=Z-

280>MnZ280>Z-1500>DSZ280>St-Z-280. Activity decreases with increasing Si/Al ratio of ZSM-5

4.6.4 Effect of ZSM-5 Si/Al Ratio

Table 4.4 shows the product yields obtained from the cracking of AL over ZSM-5s with Si/Al molar ratios of 30, 280 and 1500.

Table 4.4 Comparative MAT data at a constant conversion of 60% obtained by cracking of AL crude over Ecat and Ecat/additives

AL	E-CAT	Z30	Z280	Z1500	Mn Z280	DSZ280	St.Z280
C/O ratio	3.0	2.9	2.9	3.5	3.4	3.0	4.2
Dry Gas	2.9	6.6	3.9	3.5	4.1	4.5	5.4
H_2	0.08	0.18	0.06	0.07	0.08	0.07	0.09
C_1,methane	0.9	1.4	0.82	1.0	0.89	0.86	1.2
$C_2^=$	1.1	3.3	2.2	1.6	2.3	2.7	2.9
C_2, ethane	0.76	1.7	0.79	0.85	0.86	0.87	1.2
LPG	16.4	33.8	25.1	23.5	26.6	26.3	27.8
$C_3^=$	5.1	6.8	9.7	9.5	10.5	10.2	9.5
C_3	1.1	12.7	2.2	1.4	2.2	2.7	3.8
$C_4^=$	5.9	4.5	8.0	8.3	8.8	8.8	7.8
n-C_4	1.5	4.1	1.8	1.4	1.8	1.9	2.2
i-C_4	2.9	5.6	3.3	2.9	3.3	2.8	4.5
$C_2^=$ - $C_4^=$	12.1	14.6	20.0	19.3	21.6	21.6	20.2
Gasoline	50.5	29.8	40.8	42.1	39.0	39.2	35.9
LCO	18.9	15.3	16.4	17.9	16.7	16.9	15.9
HCO	9.0	12.5	11.4	9.9	11.1	10.9	12.1
Coke	1.8	2.0	2.1	2.7	2.2	2.1	2.7
HTC	0.74	2.2	0.63	0.52	0.58	0.53	0.86
$C_3^=$/LPG	0.31	0.2	0.39	0.40	0.40	0.39	0.34
C_3 olefinicity	0.82	0.3	0.81	0.87	0.83	0.79	0.71
C_2 olefinicity	0.60	0.7	0.74	0.65	0.73	0.75	0.70
%$C_3^=$/gasoline		1.7	9.4	10.5	9.4	9.0	6.0
CMR	1.0	1.2	1.2	1.2	1.2	1.6	1.2
GC-RON	72	97	74	75	65	81	71

For AL crude, the C/O ratio increased from Si/Al molar ratio of 30 to 280 then decreased for Si/Al ratio = 1500 as shown in Table 4.4. This indicates that the activity of E-Cat/ZSM-5 decreased with increasing Si/Al ratio and subsequently increased which corresponds to a drop in additive acidity [1,3,22].

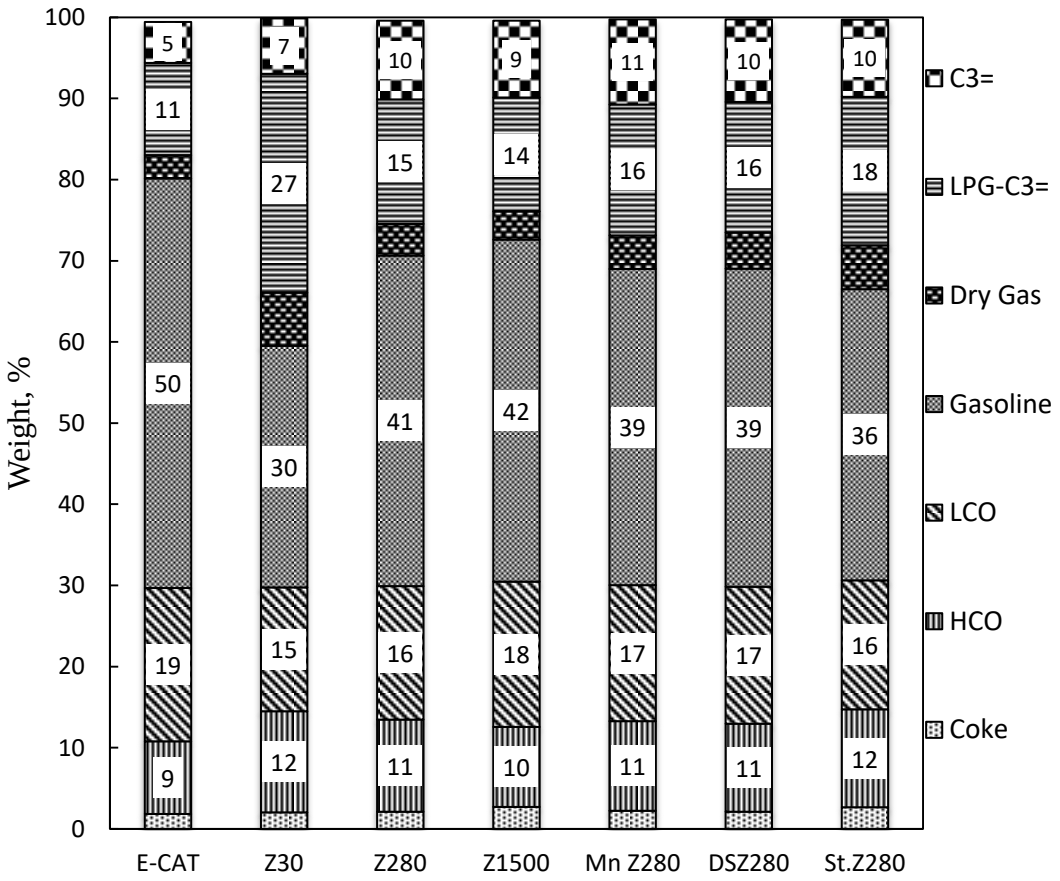

Figure 4.22 Yield patterns of cracked products for AL feed over E-Cat and E-Cat/ZSM-5 at 550 °C and 60 % conversion.

LPG yield decreased in the order of Z30 (33.8 wt%) > Z280 (25.1 wt%) > Z1500 (23.5wt %) for AL crude. Cracking of the reactive range species of the AL feed's

gasoline range hydrocarbons produces LPG [32,36]. Compared to E-Cat (16.4 wt%), the ZSM-5 additives exhibited a higher yield of LPG when used in cracking. Propylene yields increased over E-Cat/ZSM-5 compared to E-Cat for AL Crude.

Light olefins yield increased with increasing Si/Al molar ratio from Si/Al = 30 to Si/Al = 280 then reduced at Si/Al ratio of 1500 as shown in Figure 4.22. The same trend was observed for propylene yield.

The maximum yields of propylene and light olefins were obtained over E-Cat/Z280 to be 9.7 and 20 wt% respectively. The maxima trend observed for propylene and light olefins can be explained by the fact that the catalyst balances its ability to crack gasoline range species to light olefins while also preventing light olefins from saturation to paraffins [3,15].

Dry gas yield increased over Ecat/ZSM-5 compared to E-cat because of the increased ethylene yield; ethylene is formed through primary carbenium ion mechanism [28,37]. Dry gas yield also decreased with increasing Si/Al molar ratio from 6.6 wt% for Z30 to 3.5 wt% for Z1500.

Gasoline increased with increasing Si/Al ratio for Arabian Light crude cracked over all the ZSM-5 catalysts. The yield of gasoline using E-Cat only (50.5 wt%) was greater than that for any of the E-Cat/ZSM-5 catalysts. The cracking of gasoline reactive species to gaseous products is responsible for this reduction in gasoline yield [36]. The percentage increase in propylene yield per unit decrease in gasoline yield (%$C_3^=$/gasoline) is a good indication of propylene selectivity from conversion of gasoline-range olefins to light olefins and is also a critical parameter for FCC economic evaluation [3]. Compared with E-Cat only, for AL Crude, the %$C_3^=$/gasoline ratio showed the following trend: Z30 (1.7)

< Z280 (9.4) < Z1500 (10.5). The increase in $\%C_3^=$/gasoline ratio with increasing Si/Al molar ratio could be as a result of changes in the density and strength of ZSM-5 acidity [32].

Coke yield increased with increasing Si/Al molar ratio from 2.0 wt% for E-cat/Z30 to 2.7 wt % for Z1500. The amounts of HCO in the product decreased slightly from Si/Al = 30 to Si/Al = 1500, while LCO in the product increased for the same range. Both LCO and HCO yields with E-Cat/ZSM-5 catalysts were close to the yields obtained from using only E-Cat.

The composition of gasoline (paraffins, olefins, naphthenes and aromatics) in the fresh feeds and cracked products over E-Cat and E-Cat/ZSM-5 at 60 % conversion is shown in Figure 4.23. The AL crude has a paraffin content of 64.5 wt%, 26.9 wt% aromatics and no naphthenes. The paraffin in the fresh feed was cut to 33.6 wt% when cracked over E-Cat. The paraffin content of the gasoline obtained using E-cat/ZSM-5 shows the following trend: Z30 (6.44 wt %) < Z280 (29.7 wt %) > Z1500 (24 wt %). Z30 showed the greatest paraffin content because it has the highest acidity. The cracking of paraffins produces gasoline-range olefins. Over E-Cat, 29.62 wt% of olefins were obtained. Z30 (0.63 wt %) produced less olefins than Z280 (22.52 wt %) and Z1500 (33.35 wt %). The increasing trend of gasoline olefins with increasing Si/Al molar ratio of the additives can be attributed to the decreasing acidity of the zeolite additives with increasing Si/Al molar ratio [38].

The aromatics content increased from a 26.94 wt % in the feed to as high as 90.7 wt % for Z30. For E-Cat, it increased moderately to 30.11 wt %. It decreased with increasing Si/Al molar ratio: Z30 (90.7 wt %) > Z280 (37.4wt %) > Z1500 (36.8wt %). This

observation can be attributed to the difference in strong acid sites within the ZSM-5 additives. Gasoline range olefins are converted to aromatics through a series of reaction pathways involving oligomerization, hydride transfer and cyclization [22]. This transformation is catalyzed by strong acid sites, although weak acid sites do contribute but to a lesser extent. The aromatization reactions were significantly accelerated over Z30, which possesses strong acid sites compared with Z280 and Z1500 which have lower amount of strong acid sites

The GC-RON of AL feed (61) was increased to 72 over E-cat. The highest GC-RON was observed for Z30 (97). Liquid product obtained over Z280 has a GC-RON of 74 while Z1500 has a GC-RON of 75.

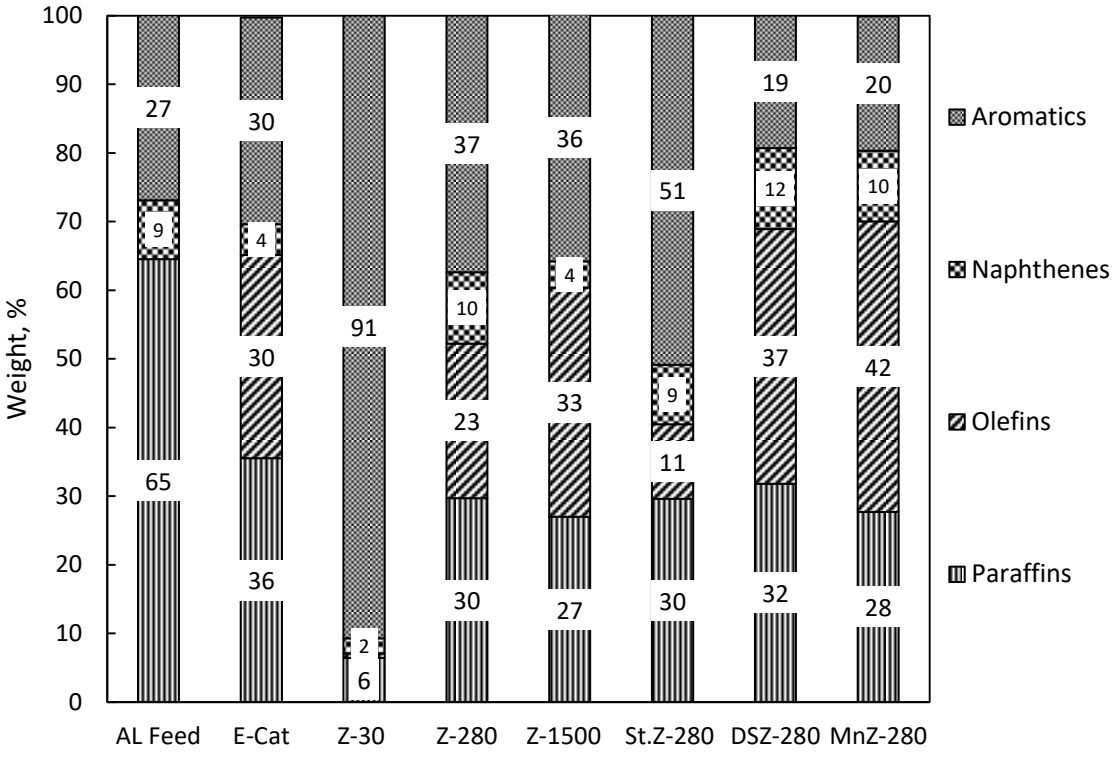

Figure 4.23 Gasoline composition of fresh and cracked AL feed over E-Cat and E-Cat/ZSM-5 at 550 °C and 60 % conversion.

4.6.5 Effect of Z280 Modification on Product Yields

Based on the MAT results of effects of cracking AL over ZSM-5 with varying Si/Al ratio and our previous investigation [35], Z280 was modified by Mn (2 wt %), alkaline and steam treatment to further enhance the yield of propylene from the cracking of AL feed.

1. Effect of Mn modification

The product yields from the cracking of AL feed over E-Cat/Mn-Z280 are shown in Table 4.4 and Figure 4.22. For 60% conversion of AL feed, the C/O ratio required when Mn-Z280 is used as additive is 3.42 compared to only 2.75 when pure Z280 is used. Slight increase in dry gas yield (3.89 to 4.13 wt %), ethylene (2.22 to 2.29 wt %) and coke (2.12 to 2.24 wt %) were observed with Mn impregnation. This increase is offset with a decrease in gasoline yield from 40.75 wt % (Z280) to 38.98 wt % (Mn-Z280).

For the liquid product, the aromatic content increased from 37.4 wt % to 45.7 wt % with Mn-impregnation, while olefins reduced from 22.52 wt % to 9.19 wt % with addition of Manganese. The paraffin content though, increased from 29.7 wt % to wt % for Mn-Z280. The change in gasoline olefins and aromatics contents may be attributed to narrowing of Z280 pores owing to the presence of MnO_2 clusters with low amount of Mn ions at the cation exchange sites [33]. GC-RON decreased from 74 to 65 with Mn impregnation of Z280.

2. Effect of alkaline treatment

The product yields from the cracking of AL feed over E-Cat/DS-Z280 are shown in Table 4.4 and Figure 4.22. A C/O ratio of 2.96 is necessary for DS-Z280 to achieve the same 60 % conversion that Z-280 attains with a C/O ratio of 2.75. Dry gas (3.89 to 4.45 wt %), ethylene (2.22 to 2.65 wt %) and propylene (9.71 to 10.2 wt %) all increased significantly

with desilication. The enhancement in propylene yield upon alkaline treatment may be ascribed to the creation of mesopores in DS-Z280 which possessed higher mesopore volume (0.33 cc/g) compared with Z280 (0.15 cc/g). The mesoporosity resulted in shortening the diffusion path and thereby decreasing the residence time, which increases the ability of catalysts to suppress the hydrogen transfer reactions by rapid elution of products [25, 39-40]. Gasoline on the other hand, decreased slightly (40.75 to 39.18 wt %) with alkaline treatment to account for the increased light olefins yield.

For the gasoline composition of the products, paraffins were higher in Z280-cracked product (29.7 wt %) than in gasoline obtained from using DS-Z280 to crack (19.84 wt %) while olefins showed the reverse trend; 22.52 wt % for Z280 and 33.1 wt % for DS-Z280. GC-RON increased with alkaline treatment from 73 to 81.

3. Effect of steam treatment

The MAT data in Table 4.4 shows that the product yields of AL cracked over Z280 and Steamed-Z280. Dry gas yield (3.89 to 5.4 wt %) and ethylene (2.2 to 2.9 wt %) increased significantly while propylene yield decreased with steaming of Z280 from 9.71 to 9.5 wt %. The gasoline yield decreased significantly from 40.75 to 35.91 wt % with steam treatment. The properties of Z280 and St-Z280 listed in Table 3 show only a drop in BET surface area in St-Z280 with no change in other properties. While dealumination by steaming leads to lowering of the number of acid sites, this disadvantage is more than offset by the creation of new types of acid sites [48]. The GC-RONs of the gasoline obtained from cracking AL over Z280 and St-Z280 were appreciably close at 73.

4.7 Comparison of Product Yields of the Arabian Crude Oils

The product yields obtained on cracking the three crude oils over the catalysts are correlated with the feed properties and compared.

4.7.1. Ease of Cracking

To compare the relative ease of cracking the three kinds of Arabian Crude Oil, the amount of catalyst required to achieve a conversion of 60% at 550°C for each crude oil is used. Catalyst/Oil ratio of 1.9, 3.0 and 3.0 are required to attain the same conversion for ASL, AXL and AL respectively. This suggests that ASL is the easiest crude to crack in the MAT amongst the three crudes. The properties of AXL and AL as shown in Table 3.1 show some similarity, and this may account for their similar ease of cracking.

4.7.2 HCO and Coke Yield

With decreasing API gravity of the crude oil feeds, the amount of coke produced by catalytic cracking increased as expected. The API gravity decreased in the order ASL (51) > AXL (39) > AL (34) while the coke make showed the following trend ASL (0.46 wt.%) < AXL (1.36 wt.%) < AL (1.8 wt.%) for cracking over E-Cat at 60% conversion for all the feeds. Also, the amount of uncracked 220°C+ fraction after processing all the feeds under the same conditions showed the same trend: ASL (22.7 wt.%) < AXL (25.7 wt.%) < AL (27.9 wt.%).

4.7.3 Extent of Propylene Enhancement

The yields and qualities of products from an FCC Unit are largely dependent on the composition of the FCC unit feed. Since a complete analysis of feedstocks aren't always available, simple gross analysis such as K-factor (UOP Characterization factor) are used

to explain trends [52]. The K-factor is indicative of the general origin and nature of a petroleum feedstock. K-factor ≥ 12 implies that the feed is paraffinic, K-factor ≤ 11.5 shows that a feed is aromatic while for $11.5 \leq$ K-factor ≤ 12, the feed is naphthenic [53].

For our crude oil feeds, ASL has a K-factor of 12.55 thus it is classified as paraffinic, AXL's K-factor is 12 which makes it paraffinic, though less paraffinic than ASL. AL, with a K-factor of 11.76 is a naphthenic feed. The effectiveness of ZSM-5 in enhancing light olefins yield is partly dependent on the naphthenic content of the feed. Because of the high hydrogen donation tendency of naphthenes, they readily produce aromatics and as a result, less-naphthenic feeds will likely show greater enhancement in light olefins yield [54].

Cracking the crude oil feeds over Z30 (which has the highest amount of acid sites among the catalysts used in this study), the percentage increase in light olefins (propylene and butenes) yield decreases with increasing naphthenic content of the feed relative to cracking over E-Cat only. Percentage increase in yield for ASL, AXL and AL are 27.5 wt.%, 14.4 wt.% and 2.7 wt.% respectively. This is because of the lower tendency of the more paraffinic feeds to form aromatics which are undesired for enhanced light olefins yield. But for the cracking of crude oils over Z280 and Z1500, the extent of light olefins enhancement increases with increasing feed naphthenes. This indicates that the effect of relatively low acidity of Z280 and Z1500 in suppressing hydrogen transfer reactions which boost light olefins yield is greater than the effect of the naphthenic content of the feeds. In fact, due to the complex nature of crude oil feedstocks used generally, the variations in the characteristics which affect product yields are more than only feed naphthenic content [54].

4.8 Kinetic Modelling

The results of the kinetic modelling of the experimental results on cracking the crude oils over E-Cat/ZSM-5 are presented in the following sections. The activation energies of the various reaction steps are calculated from the kinetic model developed.

4.8.1 Reaction Scheme

A kinetic study was conducted on the catalytic cracking of AL crude oil over E-Cat and E-Cat/Z-280 catalysts and AXL Crude over E-Cat. Crude oil consists of a large number of reactants which belong to different distillation cuts and chemical groups. Since it would be complicated to represent all the equations in a kinetic scheme, lumping of the reactants and products, based on their boiling points, is used to simplify the kinetic model [41]. For crude oil cracking, a four-lump model (shown in Figure 4.24) comprising (HCO+LCO), gasoline, gas and coke was used. Based on the composition of AL and AXL, they were divided into two fractions: (LCO+HCO) and gasoline. Assuming that much of the gasoline in the feed was unconverted [49], the cracking of (LCO+HCO) fraction was considered in the reaction scheme for modeling purpose.

The four-lump model accounted for the cracking of (LCO+HCO) to gasoline, gas and coke, as well as the cracking of gasoline to gas. The model assumes that coke is only produced from the (LCO+HCO) lump. Previous studies reported that the kinetic constants for the gasoline to coke and gas to coke reaction steps were much smaller than that of heavier reactant fractions to coke [42,43]. It was assumed that the cracking of crude oil follows second order kinetics because it is a complex mixture of hydrocarbons. The cracking of gasoline, which contains a smaller range of hydrocarbons compared to crude oil, is considered a first order reaction [43].

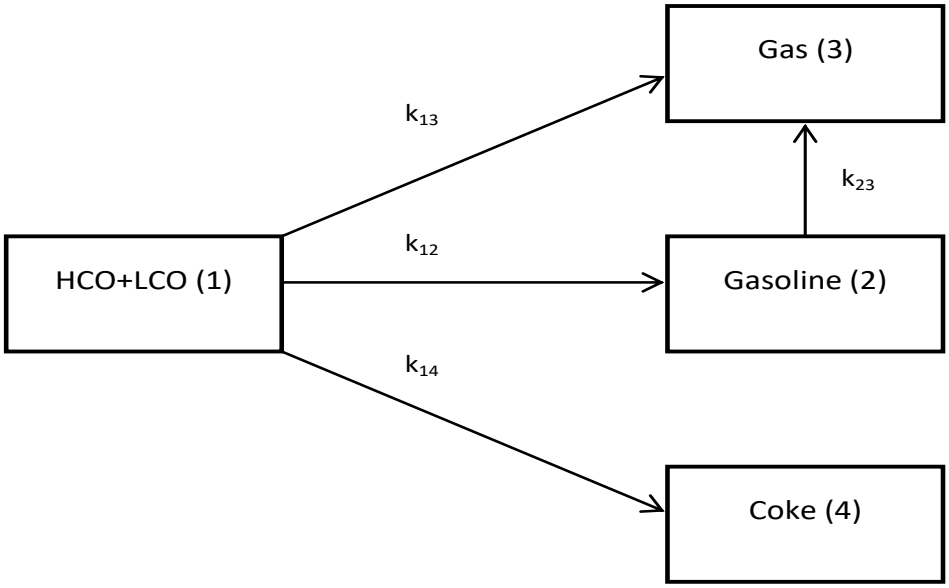

Figure 4.24 Proposed four-lump model for catalytic cracking of crude oil

Based on the proposed scheme, the governing equations representing crude oil cracking are as follows:

$$\frac{-dY1}{dt} = [k_{12} + k_{13} + k_{14}] (Y_1)^2 \varphi \quad (4.1)$$

$$\frac{dY2}{dt} = [k_{12} (Y_1)^2 - k_{23} Y_2] \varphi \quad (4.2)$$

$$\frac{dY3}{dt} = [k_{13} (Y_1)^2 + k_{23} Y_2] \varphi \quad (4.3)$$

$$\frac{dY4}{dt} = k_{14} (Y_1)^2 \varphi \quad (4.4)$$

$$\varphi = \exp(-\alpha t_{os}) \quad (4.5)$$

where φ is the catalyst decay function which accounts for the loss in catalytic activity due to coking. It is represented by an exponential decay function shown in Equation (5). It

depends on the time-on-stream (t_{os}) which is 30 seconds for this kinetic study. For simplicity of the model, it is assumed that the deactivation function φ is the same for all the reaction steps. This is because the cracking of crude oil and gasoline takes place on the same acidic sites and is hence subjected to similar levels of coke deactivation. k_{ij} in the rate equations are temperature dependent rate constants that are represented by Arrhenius formula given as:

$$k_{ij} = k_{0,ij}\exp\left[\frac{-Eij}{R}\left(\frac{1}{T} - \frac{1}{T0}\right)\right] \qquad (4.6)$$

T_o in Equation (6) is the centering temperature which is incorporated to reduce the interaction between parameters [45]. Isothermal reactor conditions were also assumed because of negligible temperature changes observed during the reactions.

4.8.2 Determination of model parameters.

Non-linear regression analysis with least squares method was used to determine the kinetic parameters for crude oil cracking over catalysts. The rate equations (1) to (4), deactivation function (5) and Arrhenius equation (6) were solved together using MATLAB ODE 45- 4th order Runge-Kutta and Least Squares Curve Fitting 'lsqcurvefit' routine. The centering temperature T_o in Arrhenius relation was set equal to 512.5 ºC. The sum of squares of the differences between the calculated and experimental values of the mass fractions of the reactants and products were minimized by the optimization criteria defined in the MATLAB routine. The data points used for the kinetic study were selected from a range of C/O ratio of 1 to 4 at four reaction temperatures (475, 500, 525 and 550 ºC).

Figure 4.25 shows the predicted and experimental conversions versus temperature for cracking AXL over E-Cat. The experimental and predicted conversions were reasonably

close for all C/O ratios at all the temperatures. Experimental and predicted yields match considerably for AXL cracking over E-cat as shown in Figure 4.25.

Figure 4.27 and Figure 4.29 show the predicted and experimental conversions versus temperature for cracking AL over E-Cat and E-Cat Z280 respectively. The experimental and predicted conversions were reasonably close for all C/O ratios at all the temperatures. Experimental and predicted yields match considerably for AL cracking over E-cat and E-cat/Z-280 as shown in Figure 4.28 and Figure 4.30.

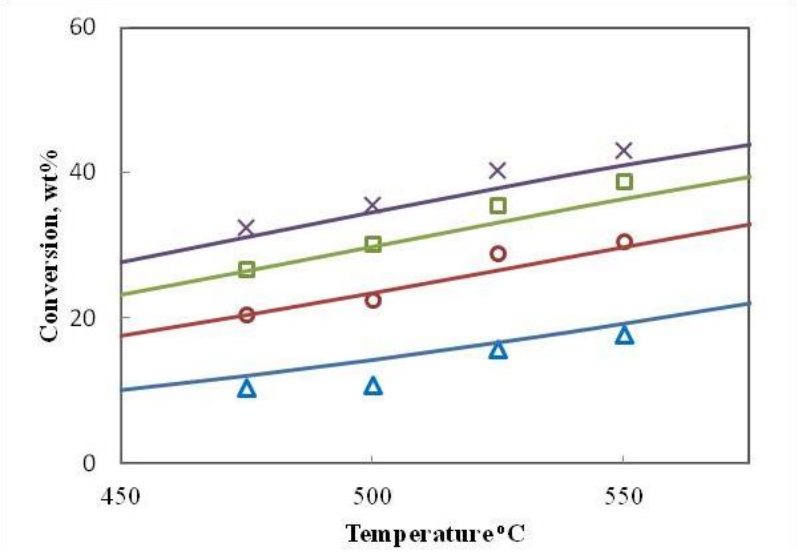

Figure 4.25 Predicted (lines) and experimental (symbols) conversion at C/O of (Δ)1,(○)2, (□) 3 and (×) 4 for AXL Cracking over E-Cat

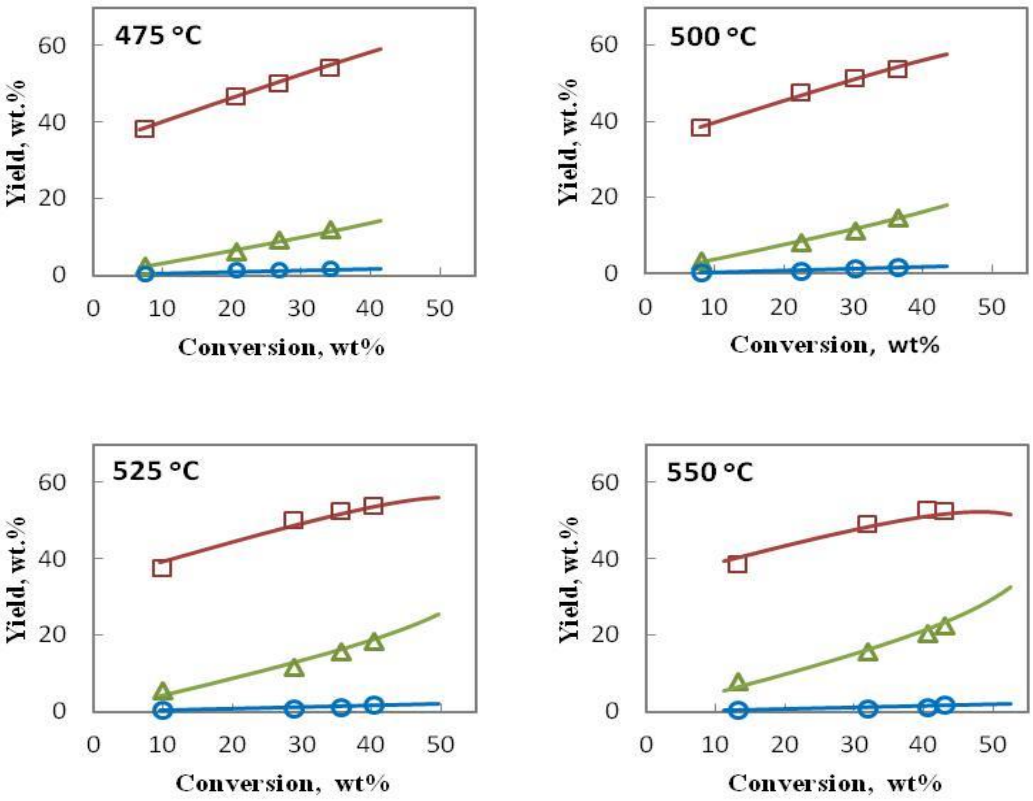

Figure 4.26 Predicted (lines) and experimental (symbols) yields of (□) gasoline, (Δ) gas and (○) coke for AXL cracking over E-Cat

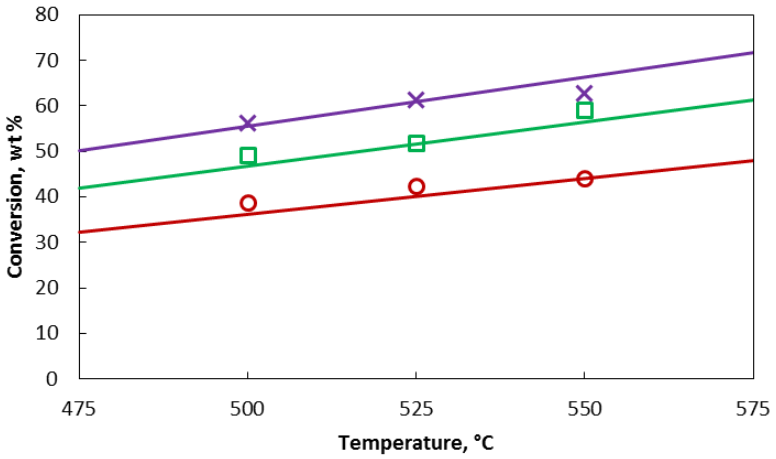

Figure 4.27 Predicted (lines) and experimental (symbols) for cracking of AL over E-Cat at C/O of (Δ)1;(○)2; (□) 3 and (×) 4

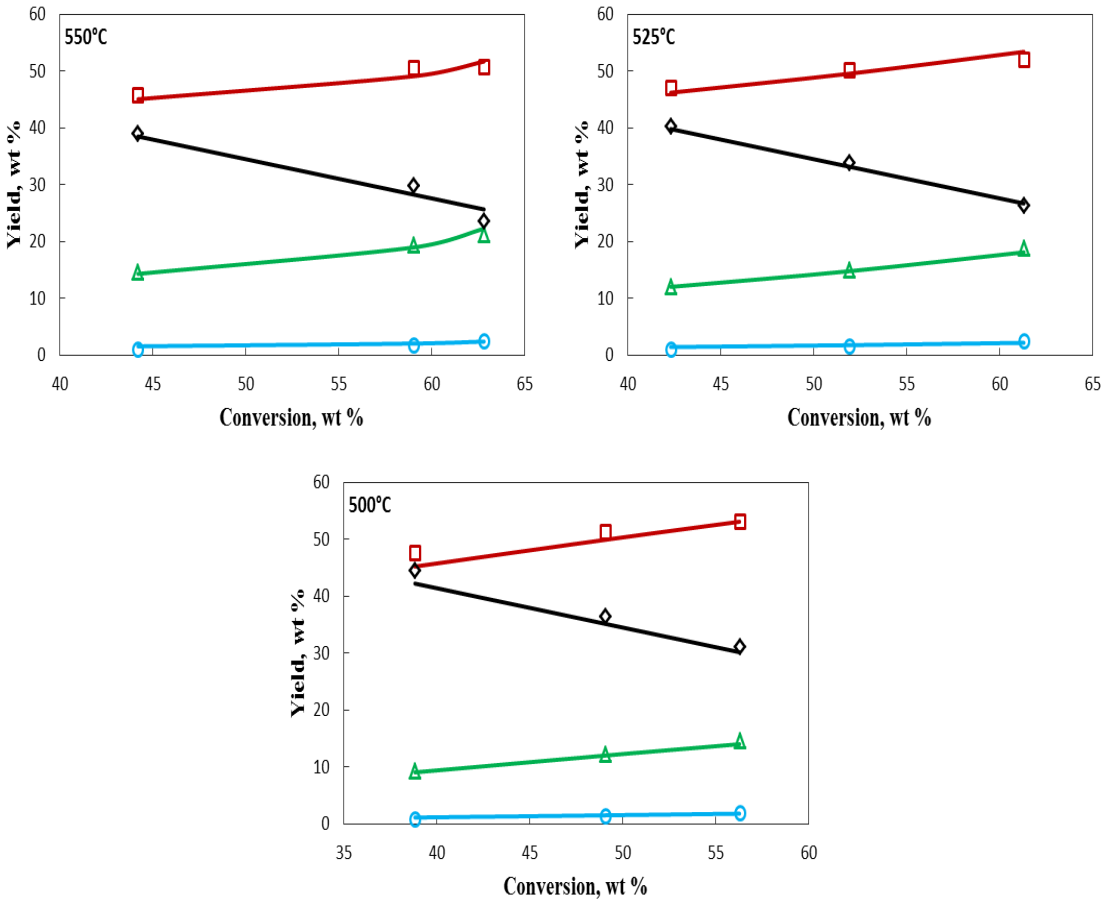

Figure 4.28 Predicted (lines) and experimental (symbols) yields of (♦) HCO+LCO; (□) gasoline; (Δ) gas and (○) coke for cracking of AL over E-Cat

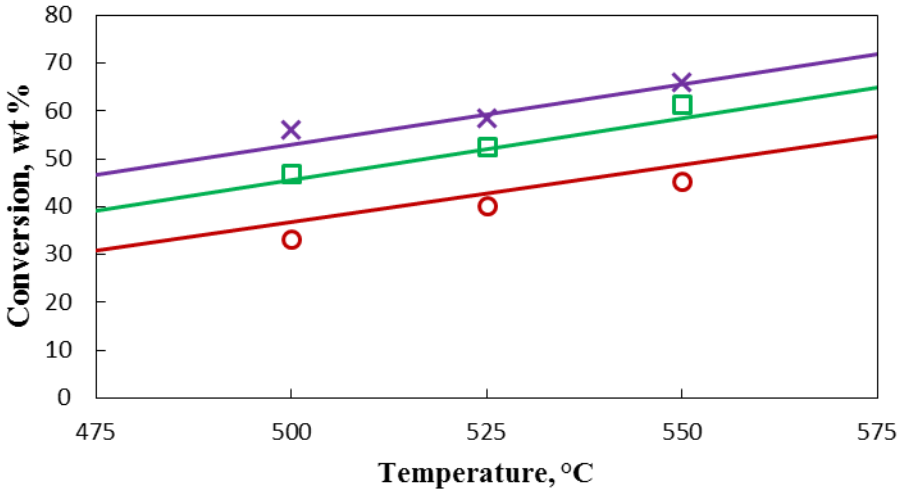

Figure 4.29 Predicted (lines) and experimental (symbols) for cracking of AL over E-Cat/Z-280 at C/O of (Δ)1;(○)2; (□) 3 and (×) 4.

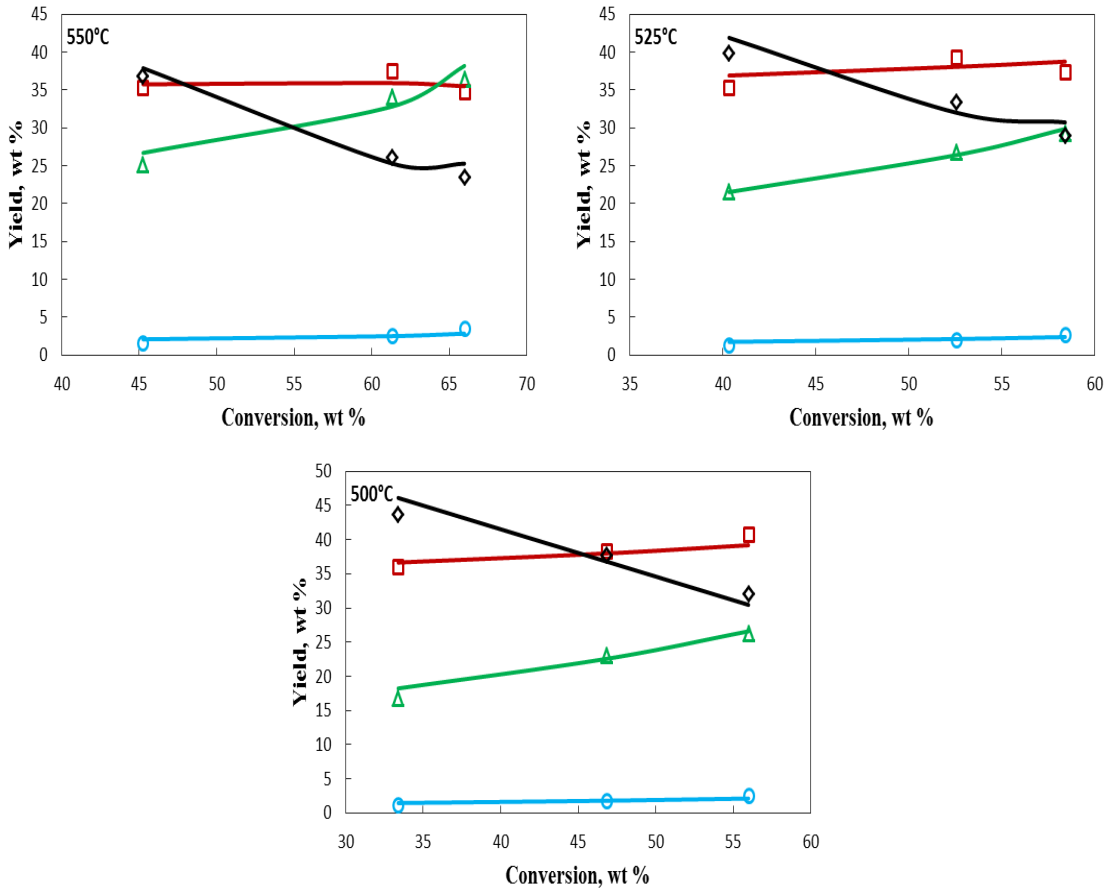

Figure 4.30 Predicted (lines) and experimental (symbols) yields of (♦) HCO+LCO; (□) gasoline; (Δ) gas and (○) coke for cracking of AL over E-Cat/Z-280

The rate constants and activation energies estimated for all the reaction steps considered for AL and AXL cracking are presented in Tables 4.5 and 4.6 along with their 95% confidence levels which demonstrate the accuracy level of the parameter estimates. Since activation energies for crude oil catalytic cracking are not available in the literature, comparison was made with VGO feed, as shown in Table 4.7.

Table 4.5 Estimated kinetic parameters for catalytic cracking of AXL crude oil over E-Cat

Parameter	E_{ij} (kcal/mol)	$k_{o\text{-}ij}$[a]
k_{12}	9.3 ± 0.1	37.6 ± 0.7
k_{13}	15.6 ± 0.3	24.7 ± 0.3
k_{14}	10.2 ± 0.9	2.6 ± 0.2
k_{23}	21.2 ± 1.0	1.5 ± 0.1
α (h^{-1})	21.4 ± 1.2	

[a] $k_{o\text{-}12}$, $k_{o\text{-}13}$ and $k_{o\text{-}14}$ in (weight fraction h)$^{-1}$, $k_{o\text{-}23}$ in h^{-1}.

Table 4.6 Estimated Kinetic Parameters for Catalytic Cracking of AL Feed over E-Cat

Parameter	E-Cat		E-Cat/Z-280	
	E_{ij} (kcal/mol)	$k_{o\text{-}ij}$[a]	E_{ij} (kcal/mol)	$k_{o\text{-}ij}$[a]
k_{12}	3.49 ± 0.012	49.01 ± 5.223	13.22 ± 0.015	23.84 ± 6.321
k_{13}	12.97 ± 0.018	31.49 ± 3.355	11.35 ± 0.014	42.71 ± 11.218
k_{14}	8.16 ± 0.070	3.84 ± 0.409	13.01 ± 0.016	3.97 ± 0.642
k_{23}	21.19 ± 0.271	2.05 ± 0.219	16.20 ± 0.133	6.48 ± 0.133
α (h^{-1})	30.98 ± 12.788		34.6 ± 8.743	

[a] $k_{o\text{-}12}$, $k_{o\text{-}13}$ and $k_{o\text{-}14}$ in (weight fraction h)$^{-1}$; $k_{o\text{-}23}$ in h^{-1}.

Table 4.7 Comparison of activation energies for AXL and AL cracking with literature values for VGO cracking.

Reaction Step	Activation Energies, kcal/mol							
	Present Study (AXL)	Present Study (AL)	Schwaab et al. [45]	Ancheyta-Juarez et al. [41]		Wielers et al. [50]	Ch et al. [46]	Ahari et al. [51]
E_{12}	9.3	3.5	13.7	28	8.1	13.7	16.3	14.3
E_{13}	15.6	13	15.7	24	8.5	11.2	21.3	11.4
E_{14}	10.2	8.2	7.6	16	17.9	7.6	15.4	7.4
E_{23}	21.2	21.2	12.6	34	13.3	10.2	12.6	16.5

Cracking Arabian Light Crude over E-cat, the apparent activation energies for the conversion of AL to gasoline (E_{12}) and gas (E_{13}) were obtained as 3.5kcal/mol and 13 kcal/mol respectively (Table 4.6). Over E-cat/Z-280 the corresponding values were 13.2kcal/mol and 11.4kcal/mol for E_{12} and E_{13} respectively. Increased apparent activation energies for AL cracking over E-Cat/Z280 compared E-Cat show that it is easier to crack AL crude over the former catalyst than the latter one. Conversely, the apparent activation energy for the conversion of gasoline to gas (E_{23}) decreased from 21.2kcal/mol for E-Cat to 16.2kcal/mol over E-Cat/Z-280. This signifies that gasoline gets converted to gases easier over E-Cat/Z280 than over E-Cat only.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Background

This chapter summarizes the findings of this thesis and gives recommendations for future works in the cracking of whole crude oil

5.2 Conclusions

This study has demonstrated the possibility of cracking Arabian Super Light (ASL), Arabian Extra Light (AXL) and Arabian Light (AL) crude oils into light olefins and high aromatics gasoline under conventional FCC conditions. All the additives used in this study increased the light olefins yield relative to using only E-Cat at similar temperatures and conversion levels. At a temperature of 550°C and a constant conversion of 60% for all the feeds, the light olefins yield increased with Si/Al molar ratio up to a maximum (at Si/Al = 280) and decreased subsequently. The maximum light olefins yield obtained for ASL, AXL and AL were 14.5 wt%, 21.3 wt% and 20 wt% respectively over E-cat/Z-280.

Modification of the ZSM-5 additive with Si/Al molar ratio by manganese impregnation, desilication and steaming only lead to slight increase in the light olefins yield for all the feeds when cracked at 550°C and similar conversion level of 60%. For the three crude oils cracked in the MAT, the light olefins yield over desilicated Z280 (E-Cat/DSZ280) were 15.7 wt%, 23 wt% and 21.6 wt% for ASL, AXL and AL respectively.

At a constant conversion of 60% and temperature of 550°C, gasoline yield decreased with increasing Si/Al molar ratio for all the feed. Over E-Cat/Z280, the gasoline yield was

53.9 wt%, 40.6 wt% and 40.8 wt% for ASL, AXL and AL respectively and their corresponding GC-RONs were 71, 64 and 74. Modification by Mn impregnation, steam treatment and desilication led to slight reductions in the gasoline yield with minimal changes in their GC-RONs. The gasoline aromatics content for the feed increased in the following order: ASL (25.4 wt%) < AL (37.4 wt%) < AXL (48.4 wt%)

With respect to the crude oils used, for all the conversion levels, at all temperatures, the yield of light olefins increased in the order ASL < AL < AXL. At 550°C and 60% conversion, the light olefins yield for the cracking of the feeds over E-Cat/Z-280 were ASL (14.5 wt%) < AL (20 wt%) < AXL (21.3 wt%) while coke make showed the following trend ASL (0.61 wt%) < AXL (1.7 wt%) < AL (2.1 wt%).

The kinetic model developed predicted the product yields (gasoline and total gases) appreciably for both AXL and AL feeds. It also showed that for AL, E-Cat/Z280 requires lower activation energy (16.2 kCal/mol) for the reaction step of gasoline conversion to gases compared to cracking over E-Cat only (21.2 kCal/mol).

5.3 Recommendations

The catalytic cracking of whole crude oil is a relatively new area of research of research and as a result, there are many areas which can be improved on in future work. These can be broadly categorized under feed, catalyst and processing.

First, for the feed, the physico-chemical properties of the crude oils used should be determined in greater detail in order to explain the correlation between feed properties and product yields in Fluid Catalytic Cracking. An analysis of the composition of the feed would reveal which of the feeds would yield the largest amount of light olefins-

which is the primary objective of this work. Also, various pre-treatments should be carried out on the crude oils to ease cracking and reduce fouling.

The extent of enhancement of propylene using the modified ZSM-5 additives in this work is not substantial. Future work should focus on identifying catalyst modification techniques that are likely to have the most effect on increasing the light olefins yield from catalytic cracking of whole crude oils.

The Advanced Cracking Evaluation (ACE) unit, a more advanced reactor which represents industrial catalytic cracking units better than the Microactivity Test (MAT) unit should be used for future catalytic cracking experiments.

Finally, a detailed kinetic model which is based on the molecular compositions of the crude oil should be carried out to better understand the effects of the various zeolite additives used

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